# THE CAL-AD METHOD: A TECHNIQUE FOR THE DETERMINATION OF SURFACE ACIDITY/BASICITY

By

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# THE CAL-AD METHOD: A TECHNIQUE FOR THE DETERMINATION OF SURFACE ACIDITY/BASICITY

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A novel calorimetric-adsorption (cal-ad) method has been developed to determine the surface thermodynamic properties of solid acids. This method combines calorimetric and adsorption titrations of a slurry of the solid acid in a non-polar solvent with various basic probe molecules. The adsorption experiment is a spectroscopic determination of the amount of base remaining in solution throughout the titration. Using this information along with heats evolved over the same concentration range yields a thermodynamic description of the solid acid surface (i.e. enthalpy, equilibrium constant of binding, and number of sites for each of the different types of binding sites). The application of this method to several solid acids leads to a number of interesting conclusions. Investigating various hydration levels of silica gel enables the separation in reactivity of three different types of hydrogen-bonding sites (indicating that this method is more sensitive than all others previously used in which only one type of site was found). Another solid

investigated was a silica supported aluminum chloride superacid ($AlCl_2(SG)_n$) useful for hydrocarbon cracking reactions. This catalyst was found to contain highly acidic Brönsted sites with an absence of any Lewis acidity. The Brönsted and Lewis acidity of HY zeolites was dependant on the pretreatment temperature of the solid. A heteropoly tungstate (phosphotungstic acid) was also investigated and its acidity was also found to be dependent on the pretreatment temperature. It was also shown to contain Brönsted acidity exclusively.

# CHAPTER 1
# INTRODUCTION

## Background

The field of catalysis is of great economic importance to the chemical industry. In 1989 it is estimated that over $1 trillion worth of goods were produced using catalytic technology.[1] Recently, there has been greater emphasis placed on developing heterogeneous catalytic systems. The greatest advantage of heterogeneous systems is the ease of separation of catalyst from the reactants and products. More than 400 million barrels of oil ($8 billion dollars) per year have been saved by the use of zeolite solid acid catalysts.[2] Another advantage is the steric selectivity which can be forced on the reactants and/or the products of a reaction with a proper shape selective catalyst structure (e.g. zeolites).

The characterization of solid acids and bases has become an area of increasing interest in recent years because of their applications in heterogeneous catalysis.[3] The characterization of acid/base sites on solid surfaces is recognized as a difficult task. Shifts in infrared bands of coordinated molecules were measured and proposed to reflect acid strengths.[4,5] More recently, nuclear magnetic resonance spectroscopy has been used to study the coordination of donor molecules to the surface.[6,7] Temperature Programmed Desorption (TPD) is another technique which has gained increasing use as

an indicator of the acidity of solid acids.[8] The use of calorimetry in the past has been limited mostly to the adsorption of gaseous bases onto solids.[9] Recently, solution calorimetry has been used to measure the total heat evolved when donors are added to solid acids.[10,11] This provides an enthalpy in units of kcal $mole^{-1}$ of donor added. These measurements are difficult to interpret because the heat evolved has contributions from the amount of base complexed (i.e. the equilibrium constant), the enthalpy, and the number of sites involved. A full characterization of the solid acid would involve measuring the equilibrium constant and enthalpy of adduct formation for each of the different acceptor sites of the solid. None of the above approaches provide this information. Thus, it is not surprising to find that the measured estimates of acidity from most of these procedures fail to parallel catalytic activity.

In our laboratory, a recent approach to the characterization of solid acids, the cal-ad method, has been used to successfully distinguish two different sites for coordination of donors to a Pd/Carbon heterogeneous catalyst.[12] Conventional differential scanning calorimetry and desorption (thermal gravimetric analysis) techniques could not distinguish the sites and provided average values for interaction with the two sites. In this dissertation, the cal-ad method has been improved and used to characterize silica gel, zeolites, phosphotungstic acid, and a silica supported aluminum chloride catalyst ($AlCl_2(SG)_n$). To aid in this characterization, other physical methods (e.g. Fourier transform infrared spectroscopy and UV/vis spectrophotometry) were used. By studying the different acids with a series of bases, an E and C analysis[13] of the enthalpies of interaction yields a way to compare these acids to each other as well as all other acids

in the E and C database. This analysis is demonstrated for the solid acids and for strong acids soluble in weakly basic solvents.

## Cal-Ad Method

### Calorimetry

The calorimeter to be described consists of the calorimeter cell, a thermistor, a heater coil, an injection syringe, an electronic circuit bridge, a chart recorder, and a computer with supporting software.

Cell. The calorimetry cell is shown in Figure 1-1. It is a silvered dewer flask fitted with three joints that are used to accomodate a thermistor, a heater coil and an injection syringe. There is also another port to allow the cell to be purged with an inert gas. The maximum volume of the cell is 75 mL but smaller volumes can be used if certain precautions are taken, *vide infra*.

Thermistor. The thermistor (manufactured by Fenwal Electronics, part # 121-402-EAJ-Q01, and distributed by Newark Electronics), is fitted in a teflon plug at the end of a glass probe.

Heater coil. The heater coil is a hand-wrapped 0.5 mm diameter wire with a resistance of about 100 ohms. This coil is placed in a glass probe and mineral oil is added to a level just above the top of the coil. When the probe is inserted in the cell, it is important that the level of the oil is below the level of the solvent in the calorimeter cell. This is necessary for efficient heat transfer to the solution to obtain a valid calibration curve.

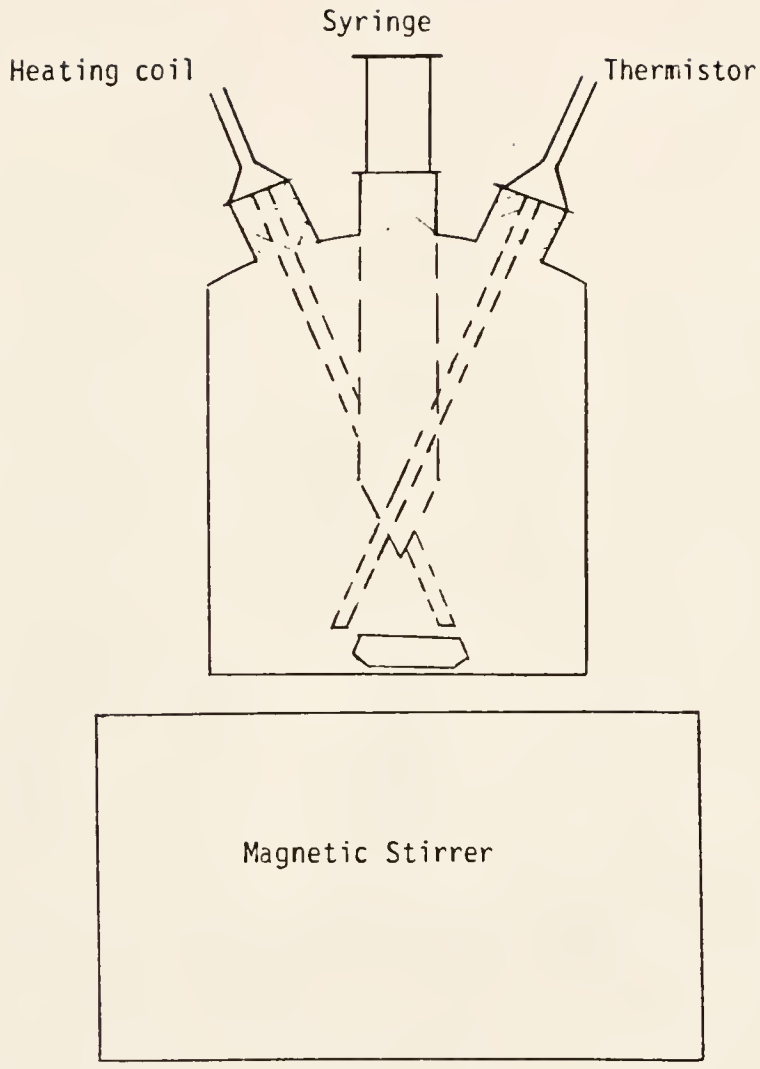



Figure 1-1. Calorimetry cell.

Injection syringe. The syringe is a Hamilton Gastight Series 1000 2.5 mL syringe with a luer tip. A glass tip is then made from a luer type outer joint with capillary wall thickness (Ace Glass, Inc.) by heating the glass and drawing it out to a tip length of about 30 cm. To accompany the syringe, there is a set of 12 brass stops which can be placed on the outside of the plunger. These stops are used, in order of decreasing length, to supply constant volume injections. The stops are calibrated by determining the injection weight of water delivered for each injection. The weight is then converted to a volume using the density of the water.

Electronics. A schematic of the electronic circuit bridge is supplied in Appendix I.

Chart recorder. The chart recorder is a Fisher Recordall Series 5000 and the chart paper used is EC-146. Chart speed is set at 2.5 cm/min and the voltage scale is set at 1.0 volt full scale.

Computer. An analog to digital board is used to link the electronic circuit bridge to an IBM Model XT personal computer. The program for data acquisition is supplied in Appendix II and a manual for the use of the program can be found in Appendix III. The Quattro (Borland) spreadsheet software was also used for data analysis.

Procedure. The solid is added to the cell in the dry box. The cell is sealed and transferred to the dry bag. Solvent is added to the cell and the syringe is filled with the injection solution in the dry bag. All the probes are placed in the cell and it is removed from the dry bag to be attached to the electronic bridge. About ten minutes is allowed for the apparatus to reach thermal equilibrium.

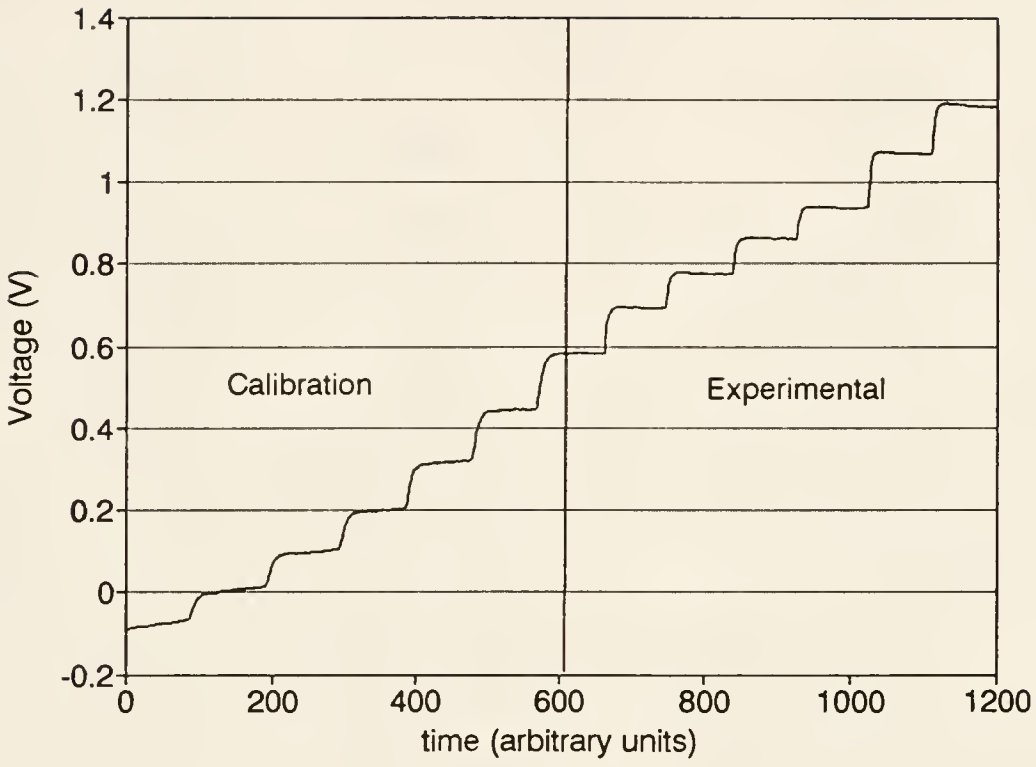



Figure 1-2. Typical calogram.

For each calorimetric titration, the heater coil and the thermistor are calibrated. A digital multimeter is used to calibrate the heater coil during the timed electronic injections of a constant voltage (5 V). By measuring the voltage over the heater coil and the voltage over a known constant resistor the power output of the heater coil can be calculated as follows:

$$P=\frac{V_H V_R}{R_R} \qquad (1\text{-}1)$$

The units of power for this calculation result in J $sec^{-1}$. Dividing this number by 4.184 J $cal^{-1}$ gives the power in cal $sec^{-1}$. The calibration of the thermistor is a linear regression of the magnitudes of the deflections caused by the timed electronic injections. A typical calogram is shown in Figure 1-2 to illustrate the deflections observed.

The experimental injections are then made by depressing the injection syringe to the next smallest brass stop. Time is allowed between each injection to allow the system to come to thermal equilibrium (a flat baseline). It is important to note that if large concentrations of base remain in solution, the heat capacity of the solvent may change significantly. This may require the recalibration of the thermistor. To test if this is the case, a timed electronic injection can be done at the end of the experimental injections to determine if it still agrees with the original calibration curve.

Adsorption

The adsorption apparatus (see Figure 1-3) consists of a 3-neck flask, injection syringe, sampling syringe, and a UV/visible spectrophotometer.

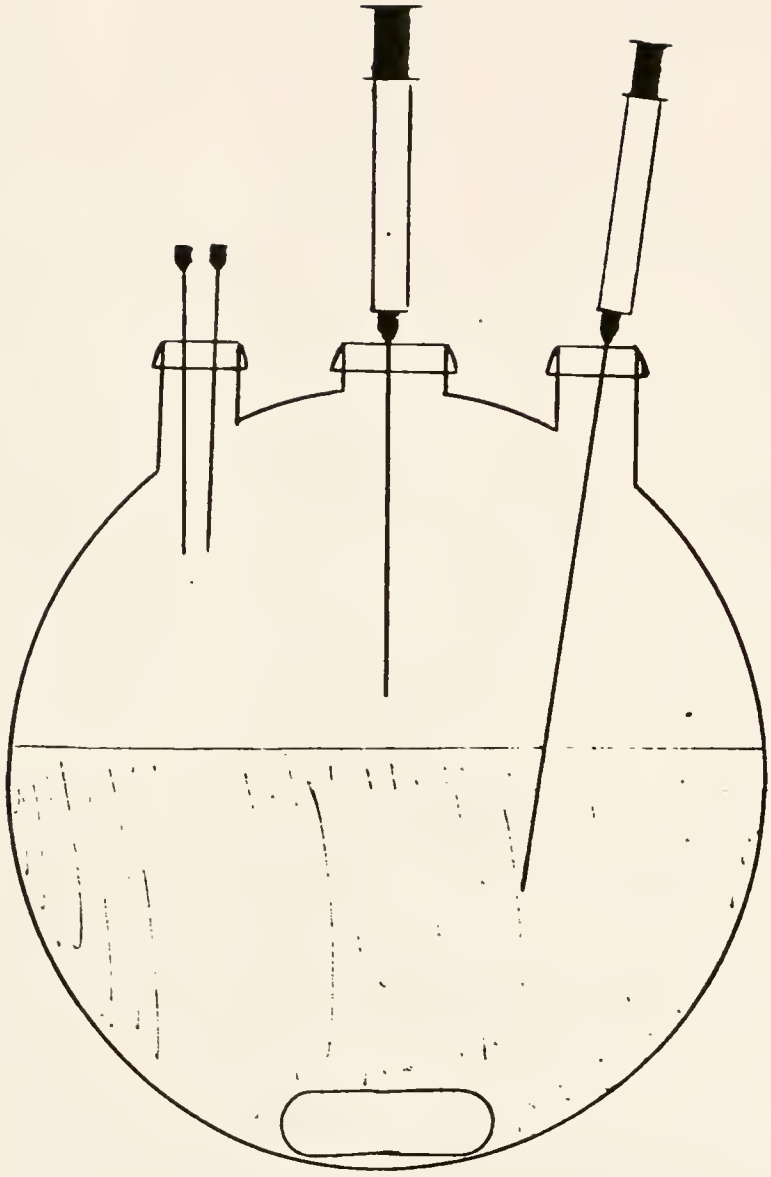


Figure 1-3. Adsorption apparatus.

Syringes. The injection syringe is the same as the one used in the calorimetry titration but in the adsorption titration, a stainless steel tip is used instead of the glass tip. The sampling syringe is a Hamilton Gastight Series 1000 1.0 mL syringe with a luer joint and a stainless steel tip.

UV/vis spectrophotometry. All spectra were obtained with a Perkin Elmer Lambda 6 UV/vis spectrophotometer. The cells used were Suprasil quartz with a 1 or 0.1 cm pathlength.

Procedure. The solid is added to the 3-neck flask in the dry box. The flask is sealed and transferred to the dry bag. Solvent is added to the flask and the syringe is filled with the injection solution in the dry bag.

While the solution is stirring, an injection is made. About three to four minutes is allowed for the system to equilibrate (same time as in the calorimetric titration). Stirring is stopped to allow the solid to settle. A sample of the solution is withdrawn and the sample volume is replaced with neat solvent. Stirring is resumed and the next injection is made. During the equilibration time for the new injection, a UV/vis spectrum can be obtained on the sample that was just removed. This sequence is repeated until all the injections have been made.

## Method

The purpose of the adsorption titration in the cal-ad method is to determine the equilibrium concentration of pyridine in solution for each added increment of pyridine in the calorimetric experiment. With the adsorption titration being separate from the

calorimetric titration, problems can arise in making a direct comparison of the equilibrium position in the two experiments. The direct comparison is necessary in order to solve the adsorption and calorimetric data simultaneously for the best K. This problem is overcome by using a constant ratio for the volume of solution/mass of solid for both measurements. An adsorption isotherm is constructed from the adsorption titration data which covers the range of base concentrations used in the calorimetric titration. The best-fit isotherm can be calculated using a modified simplex routine (Appendix IV) designed to solve the following multiple site, Langmuir type[14], equilibrium equation for a series of base concentrations.

$$S_T B = \Sigma \frac{n_i K_i [B]}{1 + K_i [B]} \qquad (1\text{-}2)$$

For i sites, $S_T B$ is the total number of moles of base adsorbed per gram of solid, $n_i$ is the number of moles of site i per gram of solid, $K_i$ is the equilibrium constant of binding at site i, and [B] is the equilibrium concentration of base in solution. In the calorimetric experiment, only the total concentration of base added is known for each calorimetric injection. The total number of moles of base on the solid ($S_T B$) is expressed as follows:

$$S_T B = \frac{([T] - [B])V}{g} \qquad (1\text{-}3)$$

where [T] is the total molar concentration of injected base and V is the volume of the experiment. By substituting Equation (1-2) into Equation (1-3) the following relationship is obtained:

$$\frac{([T]-[B])V}{g}=\Sigma\frac{n_iK_i[B]}{1+K_i[B]} \qquad (1\text{-}4)$$

The equilibrium concentration of base is measured in the adsorption experiment. In order to obtain the equilibrium base concentration for a base addition in the calorimetric experiment a preliminary Langmuir analysis of the adsorption data is carried out to give $K_i$ and $n_i$. These values of $K_i$ and $n_i$ are used to calculate the [B] corresponding to the calorimetric measurement. This allows substitution of these [B] values calculated for each base addition along with the heats obtained from the calorimetric titration into the following equation:

$$\frac{h}{g}=\Sigma\frac{n_iK_i[B]}{1+K_i[B]}\Delta H_i \qquad (1\text{-}5)$$

Where h is the heat evolved and g is the mass of the solid. Two sets of simultaneous equations are written. One set is of the form of Equation (1-5). The second set is of the form of Equation (1-2). Each set includes an equation for each base addition. The two sets are then solved simultaneously, using the modified simplex routine in Appendix IV, for the best value of $K_i$, $n_i$ and $\Delta H_i$ that reproduce the experimental quantities. It is important to note that the ratio of the volume of solution to the mass of solid (V/g) must be identical in the calorimetric and adsorption experiments. This is necessary to simultaneously solve the combined calorimetric and adsorption data sets for $n_i$, $K_i$, and $\Delta H_i$ values (i.e. the base concentration in solution relative to the amount of solid must be the same in both experiments). If this condition is not met, the data sets may be incompatible in terms of the number of different types of distinguishable sites (e.g. at a

higher V/g ratio a more reactive site could be averaged in with a less reactive site which would give rise to a faulty analysis if this data set was then used in combination with a data set obtained at a lower V/g ratio in which the two sites were separable). It should also be noted that the concentration range used in the calorimetric titration should be within the concentration range studied in the adsorption titration to avoid uncertain extrapolation of the best-fit adsorption isotherm outside of the measured range.

# CHAPTER 2
# ACIDITY OF SILICA GEL

## Introduction

Silica was chosen as the solid acid for this study because of its extensive use as a support in heterogeneous catalysis, in separations and in microelectronic fabrication. It has been studied extensively by infrared spectroscopy[15] and nuclear magnetic resonance spectroscopy.[16] Previous calorimetric investigations[10,11] of silica bonding to donor molecules assumed only a single binding site for a bases binding to the silica surface and in one study,[11] complete complexation to this site was also assumed. In the absence of equilibrium data, the units for the resulting enthalpies are kcal $mole^{-1}$ of donor added. If more than one site is involved, the enthalpy corresponds to a mole fraction average of the pyridine coordinated by the two sites. Model studies on silsesquioxanes[17] raised suspicions that sites of differing reactivity should be present on the solid depending on the extent of hydrogen bonding between neighboring hydroxyls on the surface. Isolated silanols are shown to be less acidic than clusters possessing at least three mutually hydrogen bonded hydroxyl groups in the soluble silsesquioxanes.

Using the cal-ad method we can determine equilibrium and enthalpy data for different sites on Fisher silica gel S-679 coordinating to pyridine. Furthermore, we have been able to demonstrate the dramatic influence that pretreatment of the silica has on its

reactivity. Comparison of this data with gas phase-solid data demonstrates the magnitude of the non-specific interactions that are involved when gas phase solid equilibria are measured.

## Experimental

### Purification of Materials

Fisher silica gel S-679 (LOT NO. 903424) was used as supplied. Studies were carried out on samples that were "dried" by evacuating at 28 °C, and 200 °C. BET surface areas of 590 $m^2/g$ were obtained after both pretreatment temperatures.

Pyridine (Fisher) was stored over BaO and redistilled over $CaH_2$ using a 12 in. Vigreaux column. Cyclohexane (Aldrich) was treated with activated charcoal three times in order to remove traces of benzene. It was then distilled over $P_2O_5$ and stored over 4Å molecular sieves at least 24 hours prior to use.

Reichardt's Dye (2,6-diphenyl-4-(2,4,6-triphenyl-pyridinio)phenolate), 95%, was used as supplied by Aldrich.

### Calorimetry and Adsorption

The calorimetric and adsorption titrations were carried out as described in Chapter 1 of this dissertation. A series of pyridine additions was made to provide a similar range in pyridine concentration (3.5 $\mu$M - 50 mM) for the two sets of titrations. After each addition, 3-4 minutes were allowed for equilibration. The pyridine concentration of the samples removed was determined by UV/vis spectrophotometry at 251 nm.

Ultraviolet/Visible Spectroscopy

All UV/vis spectra were obtained using a Perkin Elmer Lambda 6 UV/vis Spectrophotometer. Suprasil quartz cells of 1 and 10 mm pathlength were employed in the adsorption studies. For spectra of the solid silica, a mineral oil mull of silica was made on a piece of filter paper and referenced against mineral oil on filter paper.

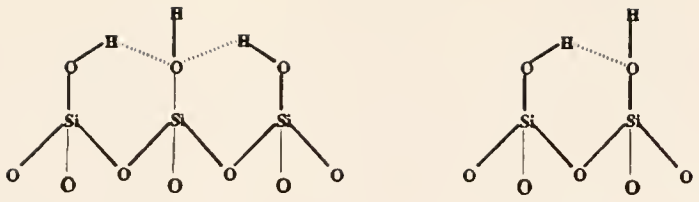
Fourier Transform Infrared (FTIR) Studies

All FTIR spectra were taken on a Nicolet 5DXB FTIR. The silica samples used in these studies were prepared by forming a slurry in cyclohexane followed by the addition of varying amounts of pyridine. The pyridine concentrations were chosen to correlate with those used in the calorimetry and adsorption titrations. The solid was then filtered after five minutes was allowed for the solutions to equilibrate. The spectrum was then obtained as a fluorolube grease GR-362 (Fisher) mull or mineral oil (Aldrich) mull on sodium chloride plates.

## Results and Discussion

Acidity of Hydrated Silica Gel

The thermodynamic data from the cal-ad analysis of the sample evacuated at 28 °C (VAC28) are shown in Table 2-1. Two different reactive sites were found with the second one being considerably weaker than the first. The enthalpy for coordination to the first site (A) is -12.6 kcal $mol^{-1}$, and that for the second site (B) is -5.3 kcal $mol^{-1}$.



A B

The fit of these results to the experimental data points is shown in Figure 2-1 which illustrates both the adsorption and calorimetric data.

In the cal-ad analysis, the pyridine concentration ranged from the smallest amount detectable to near saturation of the silica surface. The different reactive sites were discovered because both the amount of pyridine adsorbed and the amount of heat evolved were measured over this large donor concentration range. A further decided advantage of the cal-ad method is the determination of the number of active sites as 0.86 mmol $g^{-1}$ for site A and 0.86 mmol $g^{-1}$ for site B.

It is interesting to note that a simple Langmuir analysis of this adsorption data yields a different result than that obtained by the cal-ad method. The Langmuir equation:

$$\frac{[B]}{S_1B} = \frac{1}{n_1K_1} + \frac{[B]}{n_1} \qquad (2\text{-}1)$$

is solved by plotting $[B]/S_1B$ vs. [B]. The adsorption data produces a straight line (see Figure 2-2) indicating that there is 1.6 mmol/g of a single type of site with an equilibrium constant of 2700 $M^{-1}$. This is clearly inconsistent with the calorimetric data. Problems arise with this Langmuir analysis when there are two different types of adsorption sites present in nearly equal amounts, as is the case here. Since the slope of

Table 2-1. Thermodynamic parameters obtained in cyclohexane for silica-pyridine hydrogen bond formation.

| | Evacuated @ 28°C | Evacuated @ 200°C |
|---|---|---|
| $n_1$ (mmol/g) | 0.86 | 1.12 |
| $K_1$ ($M^{-1}$) | 17600 | 25400 |
| $-\Delta H_1$ (kcal/mol) | 12.6 | 5.5 |
| $-\Delta G_1$ (kcal/mol) | 5.8 | 6.0 |
| $\Delta S_1$ (eu) | -22.8 | 1.7 |
| $n_2$ (mmol/g) | 0.86 | 1.30 |
| $K_2$ ($M^{-1}$) | 320 | 580 |
| $-\Delta H_2$ (kcal/mol) | 5.3 | 3.2 |
| $-\Delta G_2$ (kcal/mol) | 3.4 | 3.8 |
| $\Delta S_2$ (eu) | -6.4 | 2.0 |

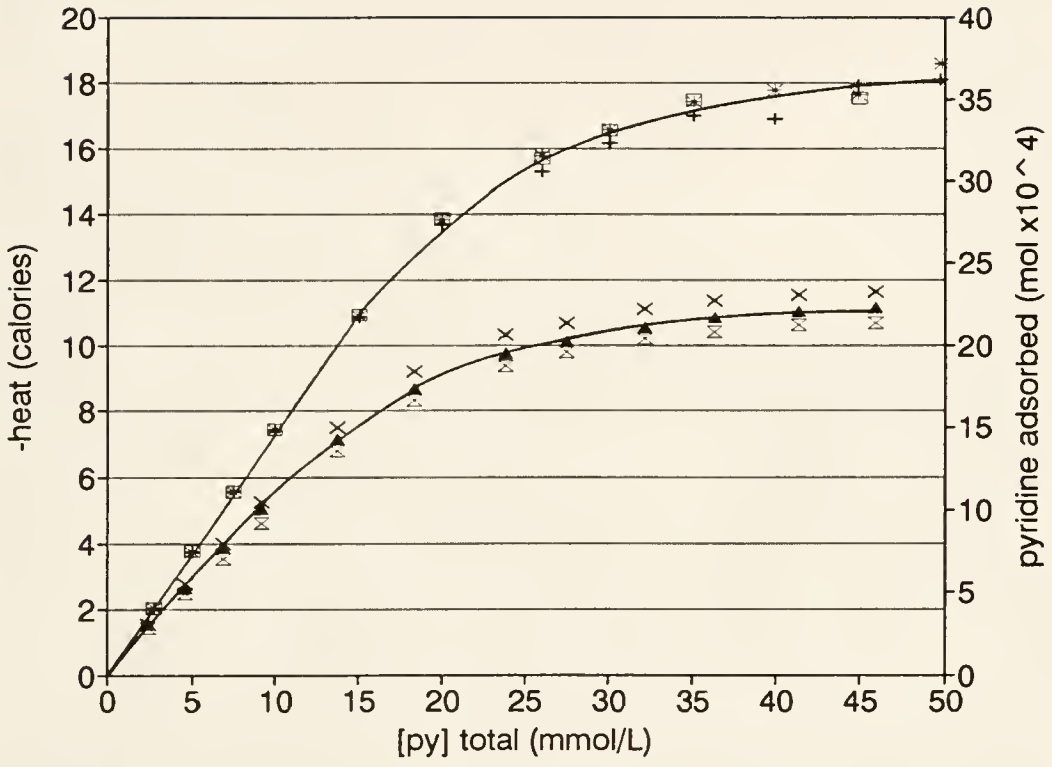



Figure 2-1. Adsorption isotherm and heat of adsorption vs. total pyridine injected for VAC28: □,*,+, adsorption data points; ▲,×,⧗, calorimetric data points; solid lines, lines calculated using values from Table 2-1.

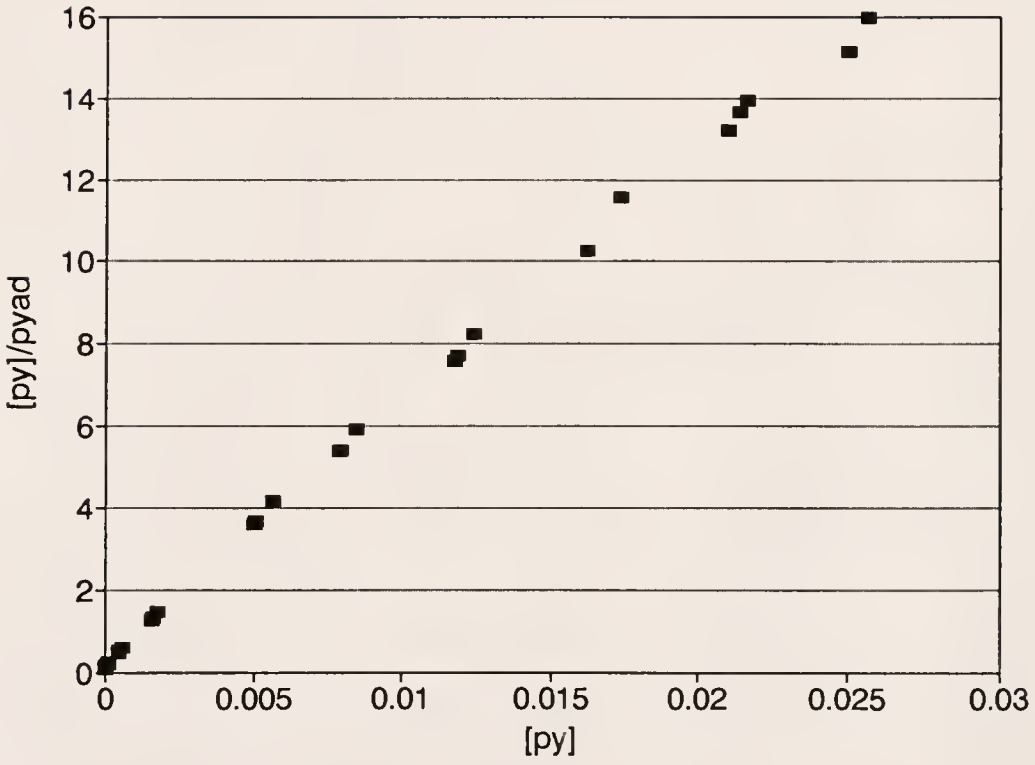



Figure 2-2. Langmuir plot of adsorption data for VAC28 is a straight line.

the line is dependent solely on the number of sites, there will be no change in the slope of the line if the two sites are present in equal quantities. By dividing Equation (2-5) by [B], another linear equation is obtained in which a plot of $1/(S_1B)$ vs. 1/[B] should yield another straight line (see Figure 2-3). This emphasizes data points taken at lower concentrations and, in the pyridine on silica case, shows curvature consistent with the two sites found by calorimetry. This serves to illustrate the difficulty in extracting meaningful data solely from adsorption isotherms.

In this system, the possibility exists that the first site involves formation of the hydrogen bond adduct and the second site involves reaction of this adduct with more pyridine to form $(C_5H_5N)_2H^+$. Accordingly, the reaction between silica and pyridine, was probed using FTIR spectroscopy. It has been reported that bands at 1447 $cm^{-1}$ and 1599 $cm^{-1}$ for pyridine adsorbed on silica gel are indicative of hydrogen-bonded pyridine.[4] Figure 2-4 shows the spectrum obtained for a silica sample at the completion of a calorimetric titration as well as the silica surface before pyridine addition. These spectra clearly show that the interaction between pyridine and the silica surface involves a hydrogen bonded adduct. Pyridinium ion is not formed, for it would be indicated by a characteristic band at 1540 $cm^{-1}$. The second site which forms in excess pyridine is also a hydrogen bonded adduct. It is significant to note that the infrared spectrum does not resolve separate shifts for the two adducts in these samples. Furthermore, the pyridine shifts upon hydrogen bonding to the strong site of VAC28 are the same as those for hydrogen bonding to the weaker sites of VAC200, *vide infra*, within experimental error.

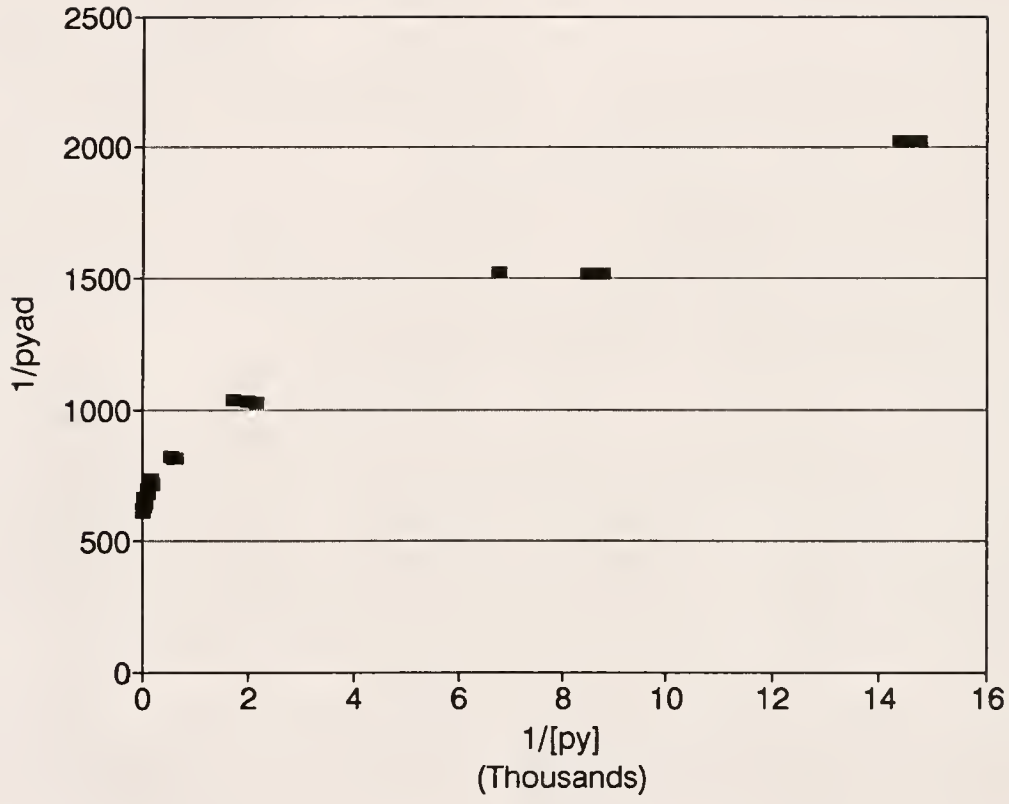



Figure 2-3. Alternate Langmuir plot showing curvature in the data.

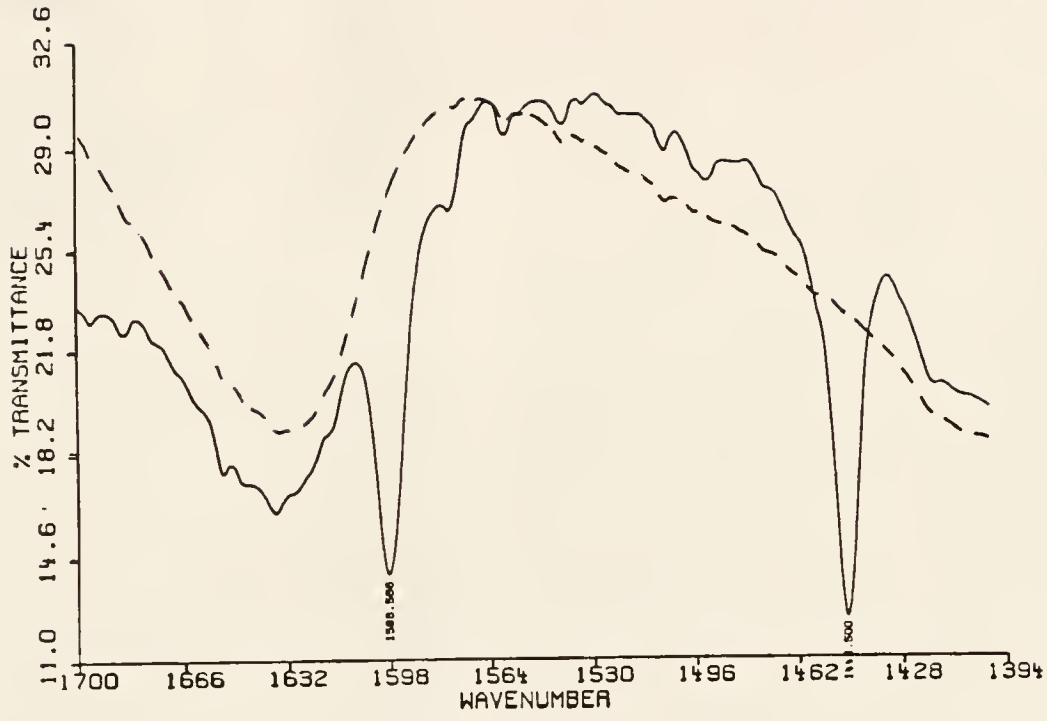



Figure 2-4. FTIR spectrum of VAC28 in a Fluorolube mull (---); spectrum of VAC28 after completion of calorimetric titration in a Fluorolube mull (—).

Arnett et al.[11] report an enthalpy of -12.37 kcal per mole of pyridine added to a silica slurry in hexane. This is not the enthalpy of adduct formation unless, at the pyridine concentrations used, all the donor is coordinated and only one site is involved. Comparison of these values with those determined for site (A) in this work indicates the extent to which these assumptions are correct. Base concentrations remaining in solution are not specified in the Arnett study,[11] but at the low base concentrations used in their work most of the donor is coordinated to the first site. Solution enthalpies for pyridine bonding to silica gel reported previously by Fowkes et. al.[10] vary from 11.3 to 12.9 kcal $mole^{-1}$. These values[10] were calculated by correcting for the base concentration remaining in solution. However, at the concentrations studied, our results show that this data has contributions from the second site averaged into the reported enthalpy. This could account for the slightly lower enthalpy values found in some systems. Since these studies were carried out on different types of silica than employed in our study, the similarity in the enthalpies of interaction indicates that similar surface sites give rise to the strong acid centers of the different samples.

Acidity of Dehydrated Silica Gel

The combined cal-ad measurements on a sample of silica gel S-679 that was pretreated by heating to 200 °C under vacuum (VAC200) were carried out next. The results of the best-fit analysis show that two different sites exist. The thermodynamic data and the values of n have been compiled in Table 2-1. The fit of the calculated concentration and heat evolved to the experimental data was similar to the fits shown in

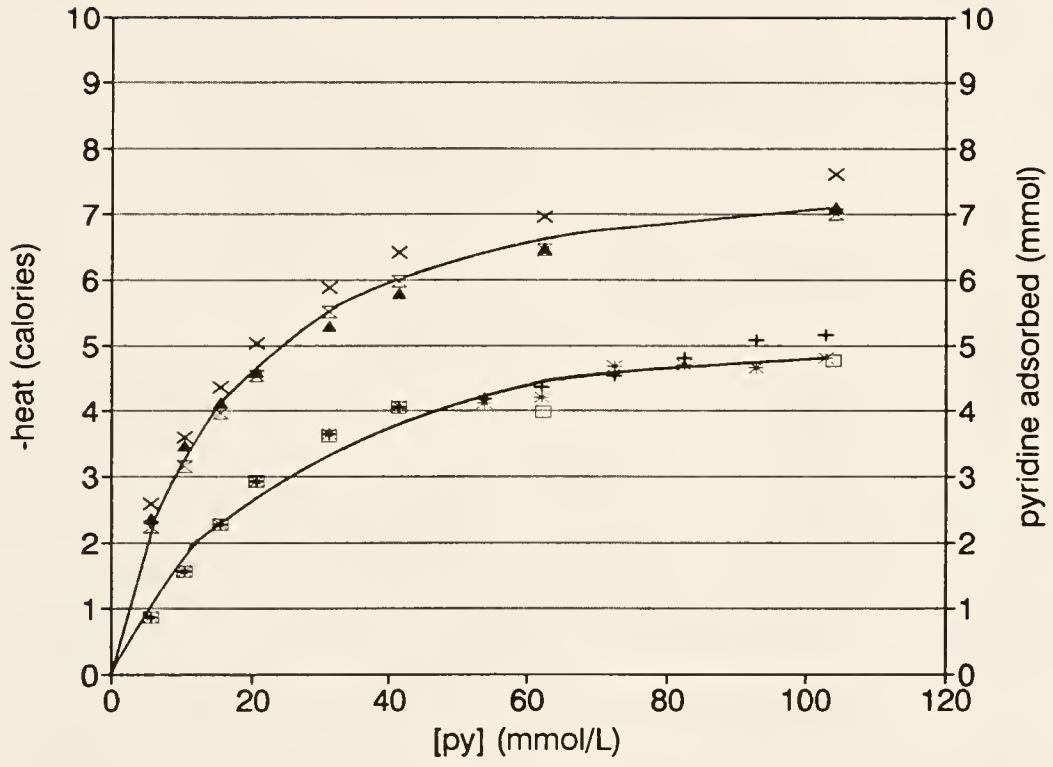



Figure 2-5. Adsorption isotherm and heat of adsorption vs. total pyridine injected for VAC200: □,*,+, adsorption data points; ▲,×,I calorimetric data points; solid lines, lines calculated using values from Table 2-1.

Figure 2-5. The enthalpy calculated for pyridine hydrogen bonding to the first site on VAC200 is similar to that found for the second site on VAC28 and is therefore attributed to a (B) type site. The difference in the entropy of adduct formation between the two different samples is very interesting and may be due to an increased propensity of the VAC200 surface to physisorb cyclohexane. The more stringent drying results in a more hydrophobic surface from loss of hydroxyl groups. Dispersion interactions which are a function of mass, are expected to be larger with silicon and oxygen atoms than with hydrogen atoms. As the number of hydroxyl groups are decreased, hydrophobicity and dispersion interactions increase. When the pyridine hydrogen bonds to the remaining hydroxyl groups of the hydrophobic solid, the surface expulsion of cyclohexane molecules into the bulk solution would lead to a positive entropy.

The above proposal is supported by infrared measurements. The FTIR spectra of VAC200 was the same as observed for VAC28 in the 1400-1700 wavenumber region. An interesting difference in the two spectra was observed in the region above 3000 $cm^{-1}$. The O-H stretching frequencies for silica, above 3000 wavenumbers, have been thoroughly studied and are quite informative. The isolated hydroxyl stretching frequencies occur at 3747 $cm^{-1}$ when studied as pellets in evacuated cells.[15] Figure 2-6 shows a spectrum in a mineral oil mull of a silica sample that was heated to 450 °C under flowing $O_2$ and then cooled to room temperature. The peak appearing at 3696 $cm^{-1}$ is assigned to an isolated silanol due to its sharpness. Hydrogen bonding to neighboring silanols leads to a significant broadening of the O-H stretching vibration.

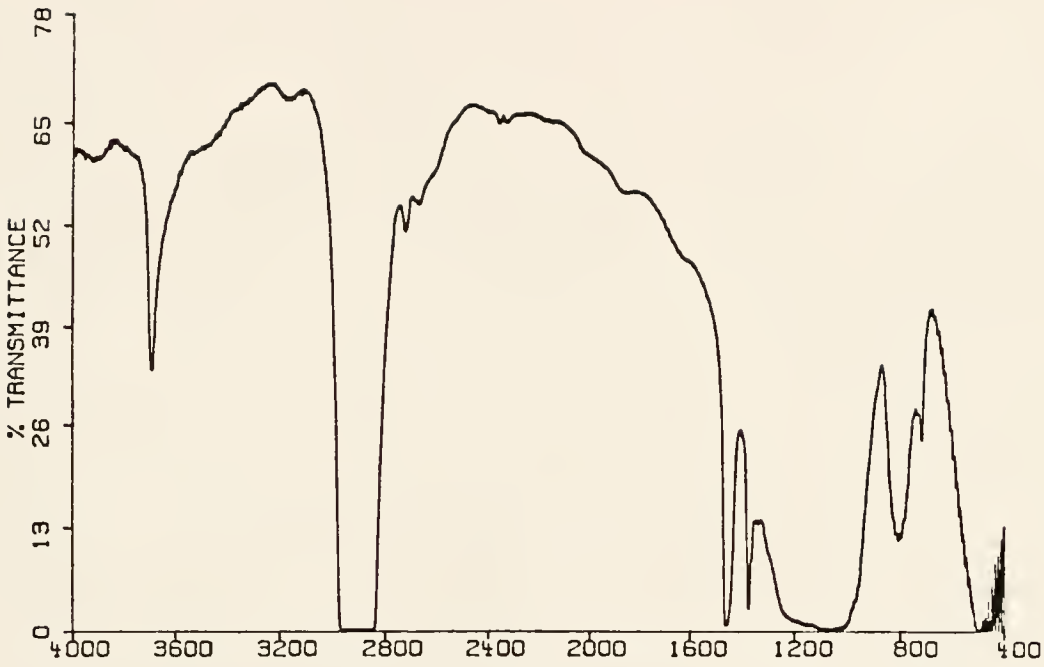



Figure 2-6. FTIR Spectrum of Fisher S-679 (after pretreatment under flowing $O_2$ at 450°C) in a mineral oil mull.

The shift from 3747 $cm^{-1}$ in vacuum to 3696 $cm^{-1}$ in a mineral oil mull is attributed to dispersion forces from physisorbed mineral oil. Absorbances from both the hydrogen-bonded and isolated silanols were present in the spectrum obtained for VAC200. The spectrum of VAC28 was less interesting in this region. Only a large broad peak was observed for the hydrogen-bonded silanols and no sharp absorbance from isolated silanols was seen.

In order to determine which silanols react first when pyridine is added, VAC200 was titrated and the FTIR spectrum recorded after each addition (Figure 2-7). A frequency decrease and broadening of the absorbance is expected when hydrogen-bond acceptors coordinate to donors. From these spectra, it is apparent that the first silanols to react are those in the hydrogen bonded region around 3500 $cm^{-1}$. Beginning with the addition of the second increment of pyridine, a slight broadening of the isolated silanol absorbance occurs indicating that they have begun to react. Reaction continues as more pyridine is added and the isolated silanol vibration broadens extensively. This substantiates our earlier proposal that the hydrogen-bonded silanols are more acidic than the isolated silanols.

An explanation for the difference in reactivity of silanol sites is suggested by solution reactivity studies on silsesquioxanes.[17] The most acidic silanol is found when three adjacent silanols are capable of hydrogen bonding to each other. Our infrared results with incremental pyridine addition indicate that the hydrogen-bonded silanols react first. The strongest site in VAC28 is as, or more, extensively hydrogen bonded than the structure shown in (A). The structure in (B) is assigned to the second site in VAC28 and

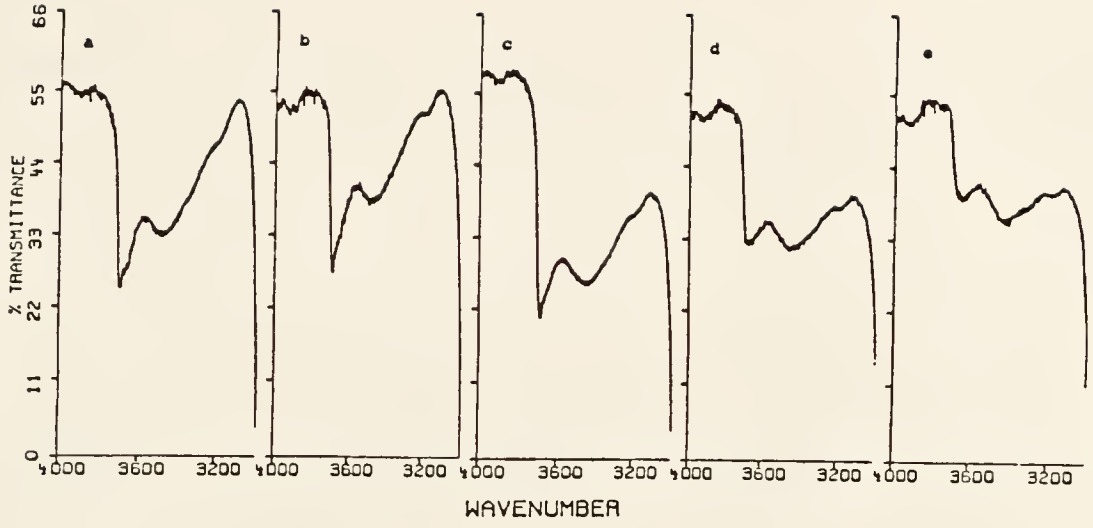



Figure 2-7. FTIR spectra of Fisher S-679 evacuated at 200°C: (a) no pyridine added; (b) 0.14 mmol/g pyridine; (c) 0.26 mmol/g pyridine; (d) 0.39 mmol/g pyridine; (e) 0.52 mmol/g pyridine.

the first, more acidic, site on VAC200. The isolated silanols (C) are weaker acids and can be assigned to the second site of VAC200. The structures for sites A, B and C are the same types of surface species proposed to arise from different pretreatment temperatures by Hench.[18]

C

There is precedence for a hydrogen bonding interaction leading to increased acidity. For example, the first ionization constant[19] of maleic acid (cis-1,2-ethylenedicarboxylic acid) is $1.4 \times 10^{-2}$ and that of fumaric acid (trans-1,2-ethylenedicarboxylic acid) is $9.3 \times 10^{-4}$. Intramolecular hydrogen bonding stabilizes the conjugate base and increases the acidity of the cis derivative. A similar explanation is offered to account for the higher acidity of silanol clusters.

Characterization of the Silica Gels with Betaine

In another attempt to find a spectral probe that would distinguish different strengths of sites on the VAC28 surface, Reichardt's Dye was adsorbed onto the silica

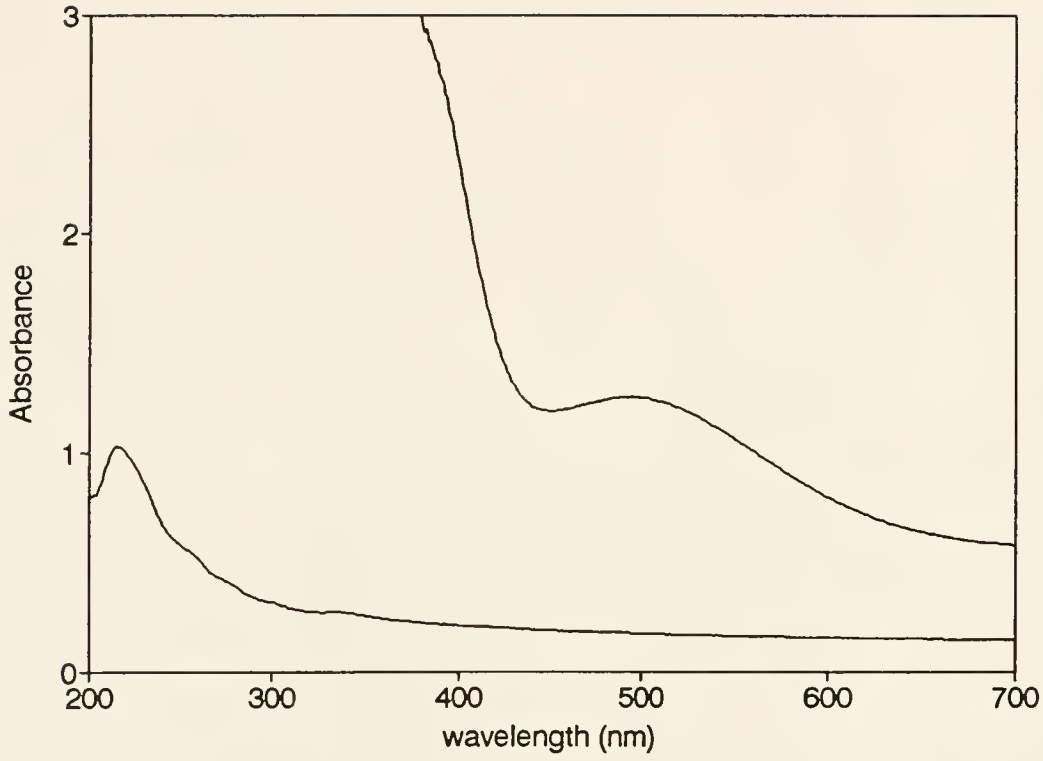



Figure 2-8. UV/vis spectra of VAC28 (bottom) and VAC28 saturated with Reichardt's dye (top).

from a methylene chloride solution. This organic dye has been used as a probe of solvent polarity and is reported to have the largest solvatochromic shift in the ultraviolet/visible region ever observed.[20] The shift in protonic solvents has contributions from a specific hydrogen bonding interaction and from non-specific solvation.[20] With silica gel, the different types of sites should shift the longest wavelength band of the dye by different amounts. This should give rise to two different absorption maxima for the lowest energy transition in the dye. Figure 2-8 illustrates the UV/vis spectra obtained for VAC28 before and after adsorption of the dye. Only one maximum is observed at 492 nm. In view of the broad adsorption bands, this probe is not able to distinguish separate sites. Furthermore, the spectrum of Reichardt's dye on VAC200 is the same as that of VAC28 within experimental error. Spectra were taken at different loadings of the dye, and though the color intensified with increased loading, the maximum in the spectrum of each sample occurred at the same wavelength. At the lowest loading, the silica was a faint red with a lot of the white silica particles. The red color continued to darken with increased loading until the surface would no longer adsorb any more dye, at which point, the red color was so intense that the silica appeared a deep purple. The observed shift of 492 nm corresponds to an $E_T(30)$ value of 58.1 kcal/mol. Since the shift of VAC28 and VAC200 are the same, betaine must be oriented on the surface in a manner that does not permit the specific hydrogen bonding of its carbonyl group to the silanol. Thus, the non-specific interaction with the silica surface is more than the combined "polar" interaction with methanol ($E_T(30)$ = 55.4 kcal $mol^{-1}$) but slightly less than that of 2,2,2-trifluoroethanol (59.8 kcal $mol^{-1}$) and water (63.1 kcal

$mol^{-1}$).[20] A larger shift occurs for the silica surface than for any polar, non-hydrogen bonding solvent e.g. $CH_3NO_2$ (46.3 kcal $mole^{-1}$).

Gas-Solid Equilibria

Extensive literature is available describing the use of temperature programmed desorption, TPD, and differential scanning calorimetry, DSC, to characterize the acidity of solids. As shown in an earlier report,[12] these methods are not as effective as the cal-ad method in distinguishing sites of different acidity. Thus, data from these studies often provide values representing a complex averaging of the different interactions. In trying to correlate reactivity, in an application that involves only the stronger sites on a series of solids, the average value provides little insight concerning the number or strength of the reactive site. A second complicating factor in ascertaining the acid-base component of the reactivity from TPD and DSC involves the added contribution to enthalpies measured with these techniques from non-specific dispersion interactions. Even in the absence of donor-acceptor interactions, a negative enthalpy will accompany the condensation of a gaseous molecule on a solid surface. This can be larger than the heat of condensation of the gaseous molecule. An indication of the magnitude of the contribution from this effect can be appreciated by comparing a recently reported enthalpy for a gas phase-solid equilibrium with that reported here for the solution-solid equilibrium.

Dumesic[21] reported an enthalpy of -22.7 kcal $mol^{-1}$ for binding of gaseous pyridine to a sample of solid Cab-O-Sil at 450 °C. A sample of Fisher S-679 silica was

pretreated as reported for the Cab-O-Sil sample. This sample preparation leads mainly to isolated silanol groups on the surface of both silica gel samples. A calorimetric titration was run in cyclohexane at room temperature employing low pyridine concentrations. An enthalpy of -3 kcal $mol^{-1}$ was measured indicating an interaction with an isolated silanol. The large difference of nearly 20 kcal $mol^{-1}$ in the cyclohexane and gas-solid enthalpy must be associated with the contribution from the non-specific dispersion interactions of gaseous pyridine with the solid surface in the gas phase-solid equilibrium. When the equilibrium is studied in a cyclohexane solution of pyridine instead of gaseous pyridine, these interactions are canceled out. A cyclohexane molecule on the solid surface of the reactants is displaced by a pyridine molecule in the adduct roughly canceling the non-specific dispersion interactions. The non-specific pyridine-cyclohexane interactions lost by the reactant leaving the solution is replaced by cyclohexane-cyclohexane interactions from the displaced cyclohexane entering solution. These solution interactions correspond to a small fraction of the heat of solution because the pyridine molecules on the surface are interacting with cyclohexane molecules at the interface.

E and C Analysis

Enthalpy values for a series of different donors bonding to silica gel have been measured by a calorimetric procedure using dilute base in hexane.[11] The reported enthalpy for the reaction of pyridine with silica gel correlated with that determined by the cal-ad method for the most acidic site on silica. As a result, reported values for the

enthalpies of adduct formation reported for the other bases can be assumed to involve only the same site and the donors can be assumed to be fully coordinated to the extent of a $\pm$ 1 kcal $mol^{-1}$ error limit. The E and C model[13] (Equation (2-2)):

$$-\Delta H = E_A E_B + C_A C_B + W \qquad (2\text{-}2)$$

has been used to interpret enthalpies of reactions in solution to determine when contributions other than donor-acceptor interactions are involved. Accordingly, it was of interest to determine if the enthalpies measured calorimetrically for coordination to silica gel were dominated by the same factors that influence bond strengths in solution. The enthalpies and reported[13c] $E_B$ and $C_B$ values for the donors are substituted into Equation (2-2) to produce a series of equations that are solved for $E_A$ and $C_A$. The $E_A$ and $C_A$ values obtained for the strongest site on silica gel are 2.30 $\pm$ 0.88 and 2.48 $\pm$ 0.15 respectively. This C/E ratio (1.08) is similar to the C/E ratio for the hydrogen bonding acceptor octanol (C/E = 1.02). It is interesting that both the $E_A$ and $C_A$ values calculated for silica are larger than the corresponding values for phenol ($E_A$ = 2.27, $C_A$ = 1.07) or trifluoroethanol ($E_A$ = 2.07, $C_A$ = 1.06). This indicates that this site on the silica is more acidic than the above organic hydrogen bonding acceptors.

The data fit is shown in Table 2-2. A good fit results indicating that the enthalpies for the adsorption of these donors by silica gel are dominated by donor acceptor interactions. These $E_A$ and $C_A$ values can be combined in Equation (2-2) with the $E_B$ and $C_B$ values reported[13c] for over 70 different donor molecules to predict their enthalpies of adsorption from cyclohexane. The enthalpies of displacement reactions can

Table 2-2 Results of E and C fit for the most acidic site on silica.

| Base[a] | $-\Delta H_{exp}$[b] (kcal/mol) | $-\Delta H_{calc}$ (kcal/mol) | Deviation (kcal/mol) |
|---|---|---|---|
| 31 Acetonitrile | 6.2 | 5.5 | 0.7 |
| 64 Tetrahydrofuran | 9.5 | 9.2 | 0.3 |
| 17 3-methylpyridine | 11.1 | (13.3)[d] | 2.2 |
| 16 Pyridine | 12.6[c] | 12.9 | 0.3 |
| 21 4-methylpyridine | 13.0 | 13.5 | 0.5 |
| 7 Triethylamine | 18.3 | 17.3 | 1.0 |
| 9 Quinuclidine | 18.3 | 18.5 | 0.2 |

[a] Numbers to the left of the base indicate their call number in the E and C database.[?c]
[b] All experimental heats were obtained from ref. 11 except where otherwise noted.
[c] From this dissertation.
[d] Omitted from the fit and calculated with the resulting $E_A$ and $C_A$ parameters.

be calculated from the differences in the enthalpies of adsorption to determine the enthalpic contribution to competitive binding. The practical applications of competition binding include separations, adhesion, removal of bound molecules and solvent selection for acid catalyzed reactions.

## Conclusions

Upon evacuation of silica, there is a change in the types of hydroxyl groups available for reaction. With mild pretreatment, there are a large number of polyhydrogen-bonded silanols which give rise to the strongest binding. Also present are monohydrogen-bonded silanols which are weaker acids than the polyhydrogen-bonded silanols. A noticeable change in the strength of the two sites occurs upon evacuation at 200 °C. At this point the polyhydrogen-bonded silanols have been effectively eliminated leaving the monohydrogen-bonded silanol as the strongest site while a new, weaker, site has appeared that can be attributed to the isolated silanol on the silica surface. The enthalpy of adsorption of donor molecules by the strongest site are dominated by donor-acceptor interactions. Gas phase-solid equilibria have shown substantial contributions to the enthalpy of adsorption from non-specific, dispersion interactions.

# CHAPTER 3
# ACIDITY OF $AlCl_2(SG)_n$

## Introduction

Recent efforts from our laboratory have produced a novel solid acid, denoted as $AlCl_2(SG)_n$.[22,23,24] The material is synthesized by a condensation reaction between aluminum chloride and silica gel in $CCl_4$. Characterization by NMR spectroscopy[23] indicates the presence of surface tetrahedral aluminum sites. Two possible structures of these surface sites are illustrated in Figure 3-1. The very strong acidity of $AlCl_2(SG)_n$ has been shown by its activity in cracking[23] and dehydrohalogenation/hydrodehalogenation reactions[25] under mild conditions where typical zeolite or silica/alumina catalysts are inactive. With a species this acidic, a better understanding of the nature of the acidity was needed. Hopefully this investigation would determine the cause of the catalyst deactivation and lead to the synthesis of a more durable catalyst.

Previous efforts to characterize the surface of the catalyst included $^{27}Al$ NMR and FTIR spectroscopy.[23] The $^{27}Al$ NMR investigation revealed the presence of tetrahedral aluminum centers in the active catalyst and octahedral aluminum in catalysts that were inactive. One of the most common methods of examining acid sites on solids utilizes the infrared spectrum of adsorbed pyridine.[4,26] Pyridine bound to Lewis acid sites

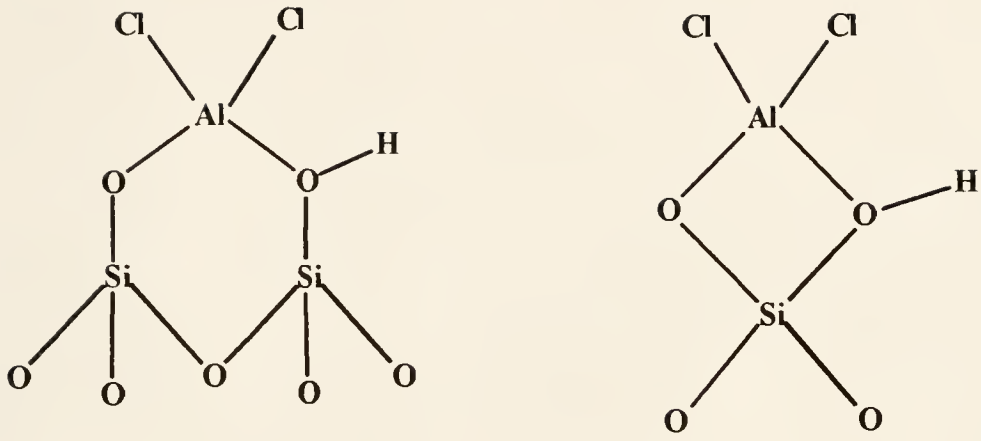



Figure 3-1. Proposed structures of $AlCl_2(SG)_n$.

(including hydrogen bonded pyridine) exhibits different spectral shifts than that for pyridinium ion arising from protonation by Brönsted sites.[4] The shift in the pyridine frequency bound to Lewis sites relative to that of free pyridine gives a qualitative assessment of acid site strengths. This procedure has been used to evaluate the acidity of $AlCl_2(SG)_n$ prepared in a series of solvents[23,27] and is found to correlate with the reactivity of the solid in acid cracking reactions.

A "spectroscopic titration" of the catalyst with pyridine would also be an important tool for the characterization of the catalyst surface. Since the pyridinium ion and Lewis bound pyridine sites have two distinctly different absorbances in the 1400-1700 $cm^{-1}$ region, incremental additions of low concentrations of pyridine can indicate the nature of the most acidic site.

Calorimetry is the most direct method of determining acidity because it yields a value for the enthalpy of interaction which is a direct measure of the bond strength of the solid acid-donor molecule adduct. The cal-ad method has been used previously to determine the surface acidity of a heterogeneous Pd/carbon catalyst[12] and silica.[28] Correlation of enthalpy changes with the spectral changes for various donor concentrations would indicate if there are different types of acid sites and which sites are most reactive. By comparing the results obtained from calorimetric titrations of $AlCl_2(SG)_n$, using pyridine and 2,6-lutidine as basic probe molecules, the contribution to the measured enthalpy from coordination to protonic and aluminum centers can be determined. Steric effects with the latter donor are expected to lead to smaller enthalpies than those for pyridine when sterically hindered, non-protonic centers are coordinated.

# Experimental

## Reagents

The $AlCl_2(SG)_n$ catalyst was used as prepared previously.[24] Pyridine and cyclohexane were purified as described earlier. 2,6-Lutidine (redistilled, 99+%) was used as supplied by Aldrich. Carbon tetrachloride was distilled over $P_2O_5$.

## Instrumentation

FTIR was performed on a Nicolet 5PC FTIR spectrometer. UV/vis spectra were obtained using a Perkin Elmer Lambda 6 UV/vis Spectrophotometer.

## Infrared Analysis

A sample of $AlCl_2(SG)_n$ is placed in a vacuum desiccator with a pyridine reservoir and evacuated to generate a pyridine atmosphere inside. The catalyst is kept in the pyridine environment at room temperature for 2 to 3 hours, during which time the catalyst changes to an off-white color. The catalyst is then removed from the desiccator and placed under vacuum for at least 2 hours to remove excess pyridine. Infrared spectra are taken as fluorolube mulls of the catalyst on NaCl plates prepared in an inert atmosphere.

The infrared adsorption titration of pyridine was conducted in an inert atmosphere of dry $N_2$. Injections of pyridine were made into a slurry of 0.10 g of catalyst in 10 mL of $CCl_4$. After about five minutes of stirring the catalyst was filtered and was allowed

to dry in the inert atmosphere. The infrared spectrum was then obtained as a fluorolube mull on NaCl plates. Pyridine loadings ranged from 1.2 mmol/g to 11 mmol/g.

Calorimetric Titrations

The calorimeter and the procedure to measure enthalpies was described in Chapter 1. The cell was loaded with 0.50 g of catalyst and 50 mL solvent ($CCl_4$ or cyclohexane) in a dry $N_2$ atmosphere. The concentrations of pyridine and 2,6-lutidine ranged from 0.2 - 50 mmol/L.

## Results and Discussion

### Infrared Examination of Adsorbed Pyridine

In order to obtain a qualitative assessment of the different acid sites for $AlCl_2(SG)_n$, the infrared spectrum of adsorbed pyridine can be used. A band at ~1540 $cm^{-1}$ involves a C-$N^+$-H bending vibration and is used as a fingerprint for pyridinium ion. A band at 1452 $cm^{-1}$ is assigned to Lewis-bound pyridine and this includes pyridine that is hydrogen bonded or bound to aluminum. A third band at 1485 $cm^{-1}$ results from both Lewis and pyridinium species. Previous FTIR characterization of this catalyst relied solely on the vapor deposition of pyridine technique[23]. This provided a spectrum in which the catalyst was saturated with pyridine. This analysis indicated the presence of Brönsted and Lewis acid sites but was unable to determine which site was stonger and presumably responsible for the catalytic activity.

Infrared Titration

Figure 3-2 illustrates the results of the infrared titration in carbon tetrachloride. Upon addition of 1.2 mmoles of pyridine per gram of catalyst, the pyridinium ion is the only species present (absorbance at 1540 $cm^{-1}$). As excess pyridine is added to the catalyst (11 mmol/g), absorbance from another species is observed. This is assigned to a hydrogen-bonded adduct since coordination to an aluminum center can be ruled out with the results obtained from the calorimetric titrations, *vide infra*.

Calorimetry and Adsorption

A non-polar solvent is utilized to elucidate the enthalpy of interaction between the $AlCl_2(SG)_n$ catalyst and pyridine. Cyclohexane is the best choice for this except the catalyst has been shown to be a good hydrocarbon cracking and isomerization catalyst.[23] Carbon tetrachloride is another good solvent except it is known to form a complex with strong electron donor amines (e.g. pyridine).[29] The results of titrations in both solvents yielded the same heats within experimental error (the value in carbon tetrachloride was corrected by adding 1 kcal $mole^{-1}$ for the heat of complex formation with pyridine). The remaining titrations were done in cyclohexane since there was no contribution to the heat from isomerization or cracking at the conditions of the calorimetric titration.

To determine the types and strengths of acid sites present on the catalyst surface, a calorimetric titration of the catalyst at low base concentrations was done. Pyridine and 2,6-lutidine were chosen as the probe bases in order to distinguish between protonic and aluminum sites. The inductive effect of the methyl groups on 2,6-lutidine make it a

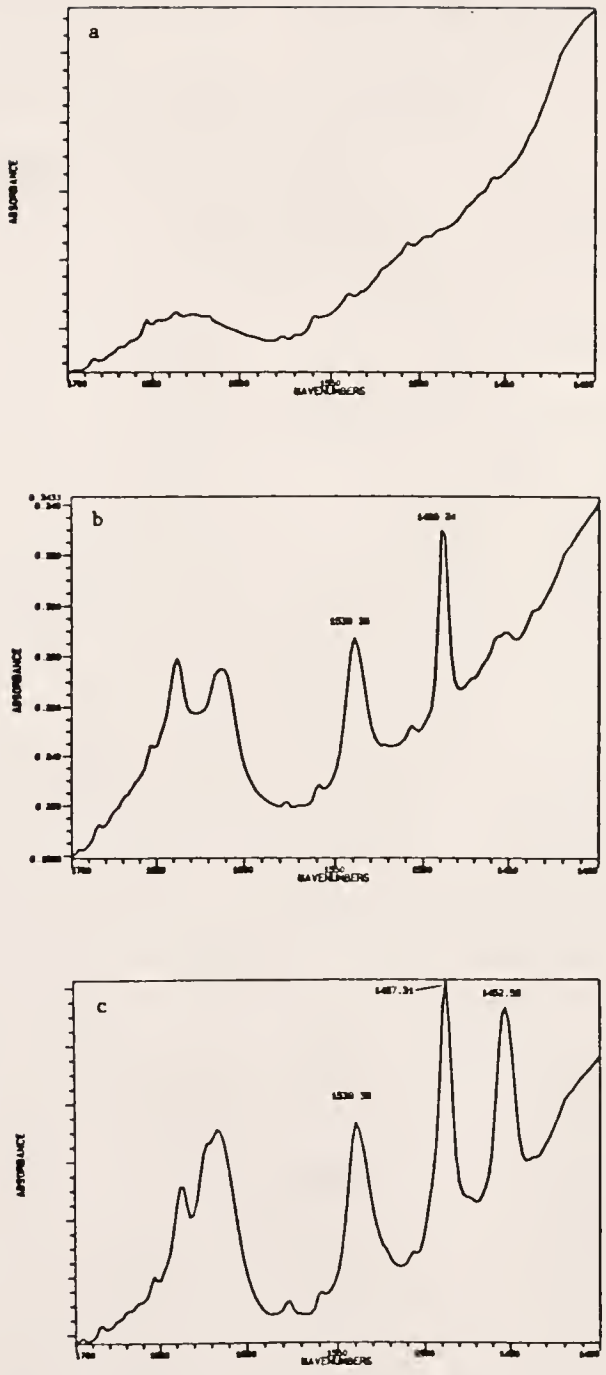



Figure 3-2. Infrared spectra obtained for the titration of active catalyst with a.) no pyridine, b.) 1.23 mmol/g pyridine, and c.) 11.3 mmol/g pyridine.

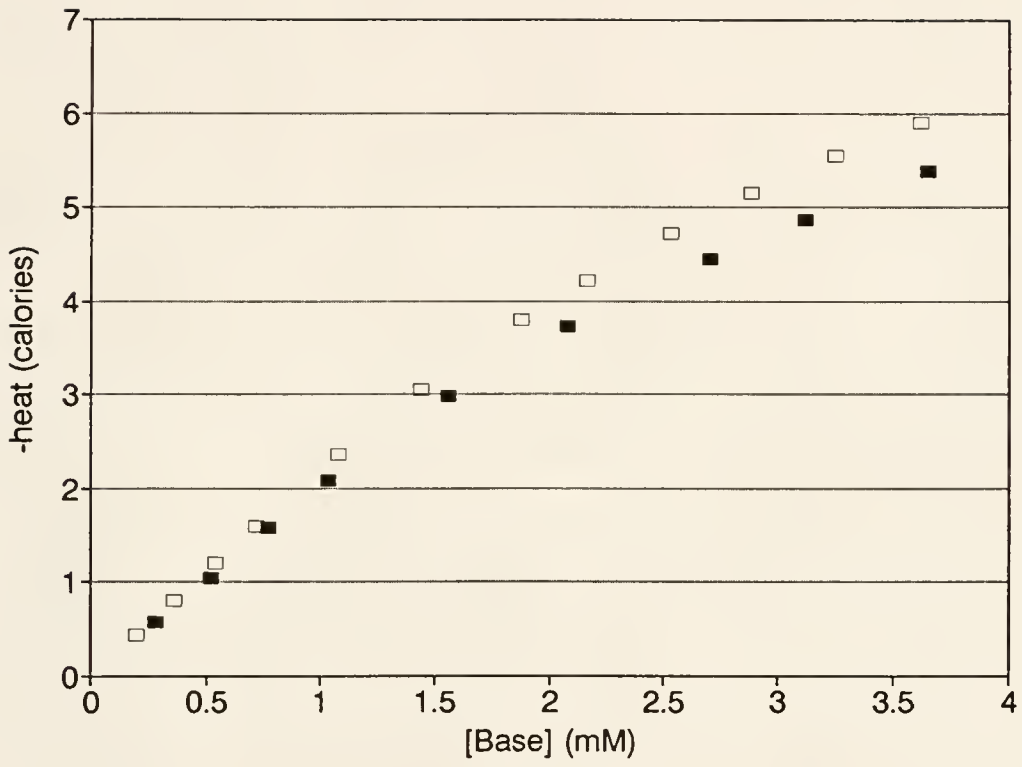



Figure 3-3. Heats evolved for active catalyst at low concentrations of pyridine (■) and 2,6-lutidine (□).

slightly stronger donor than pyridine. However, the methyl groups result in steric hinderance with acceptors larger than the proton resulting in a weaker interaction. Figure 3-3 shows the similarity in reactivity between the two bases. This titration rules out the possibility of any Lewis acidity other than hydrogen bonding, since the enthalpy of adduct formation for 2,6-lutidine is slightly higher than the enthalpy for pyridine. Steric constraints are expected with 2,6-lutidine toward an aluminum acceptor center and would lead to a reduced enthalpy for this donor compared to pyridine if such centers were involved. It is obvious from this experiment that the acid sites on the catalyst are protonic and are very strong.

By assuming that the pyridine is completely complexed (a necessary assumption due to the adsorption results, *vide infra*), an enthalpy can be calculated for each addition of base. This enthalpy is calculated by dividing the amount of heat for each injection by the number of moles of base added for that injection, yielding a value in kcal (mol base added)$^{-1}$. Figure 3-4 is a plot of the calculated enthalpies vs. the total amount of base added. We see from this graph that the first site has a $\Delta H$ = -40 kcal (mol pyridine added)$^{-1}$. This interaction is considerably stronger than the -28 kcal mol$^{-1}$ enthalpy of adduct formation between trimethylaluminum and pyridine and much larger than the -12.6 kcal mol$^{-1}$ interaction of pyridine with silica gel. It is also interesting to note that there is a second plateau in the calculated enthalpies. This is an indication of a second type of acid site on the catalyst with a $\Delta H$ = -20 kcal (mol pyridine added)$^{-1}$.

In order to quantify the acid sites present on the catalyst, the cal-ad method was attempted. This involves the combination of calorimetric and adsorption titration data

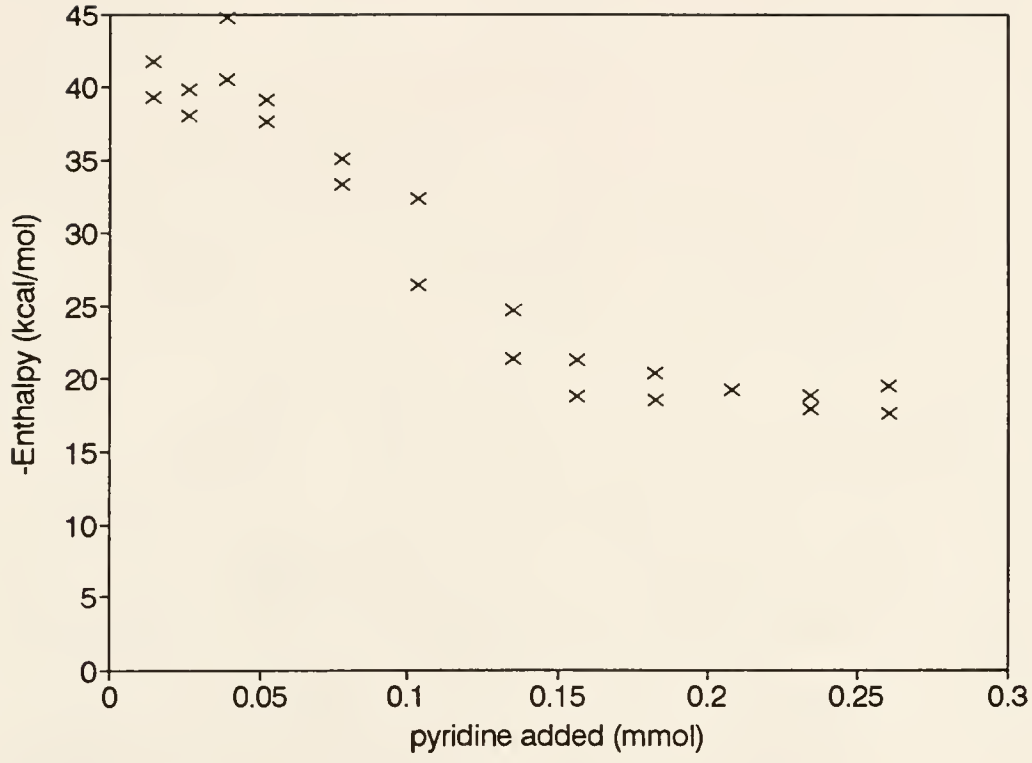



Figure 3-4. Enthalpies calculated assuming full complexation of the base.

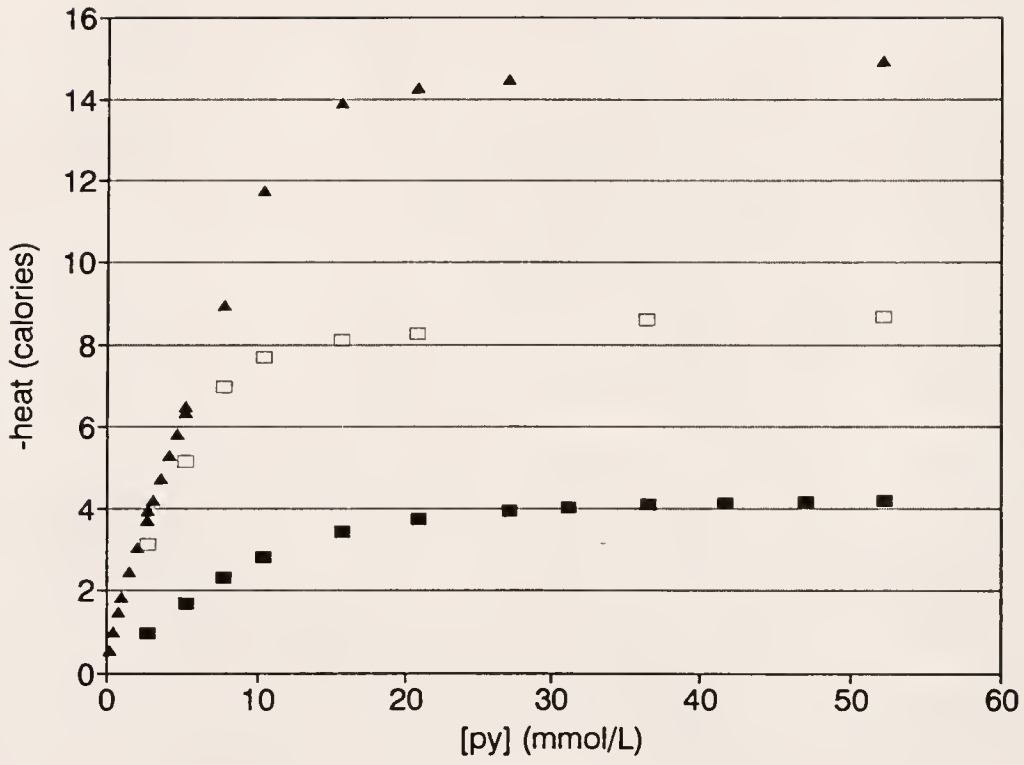



Figure 3-5. Heats evolved over a large concentration range of pyridine for silica support (■), active catalyst (▲), and deactivated catalyst (□).

over the entire concentration range in which the catalyst adsorbs the base. Figure 3-5 shows the results of the calorimetric titration of the active catalyst over a large pyridine concentration range. A catalyst which has been deactivated in a flow reactor by allowing a constant flow of $N_2$ to pass over it for 24 hours at room temperature (this treatment resulted in the loss of HCl and reduced the activity of the catalyst) is also shown. The deactivated catalyst has undergone a loss in the number of acidic sites resulting in the reduction of the total heat evolved in the titration. A small number of the active sites remain in the deactivated catalyst as indicated by the heat evolved at low pyridine concentration.

The adsorption titration produced an interesting result. An initial addition of 0.14 mmoles of pyridine to 0.5 grams of catalyst in 50 mL of cyclohexane was made. This was allowed to come to equilibrium and the UV/vis spectrum was taken of a sample of the solution above the solid (see Figure 3-6). This spectrum indicated that there was no pyridine in solution but there was a small amount of a new species present at longer wavelength (267 nm). Appearance of this band was accompanied by an increase in base line adsorbance at all wave lengths most likely due to small solid particles in the solvent. At this amount of added pyridine, (nearly 0.3 mmol/g), the FTIR spectrum of the solid catalyst shows that the pyridinium ion is formed at this concentration (Figure 3-2). As successive additions of pyridine are made to the solid in cyclohexane, the absorbance at 267 nm increases. When the amount of pyridine added reached 1.6 mmol/g, free pyridine was found in solution (absorbance at 251 nm). At this and higher pyridine concentrations, the absorbance at 267 nm did not increase.

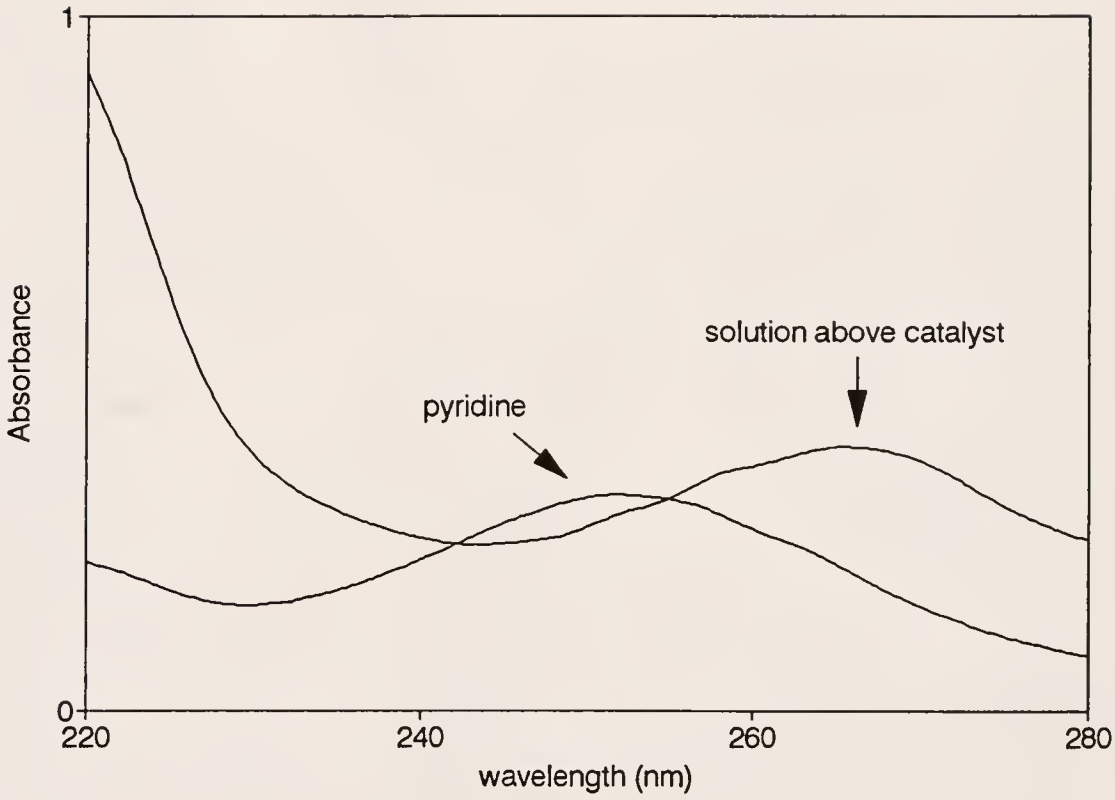



Figure 3-6. UV/vis spectrum of solution above catalyst after 0.14 mmol/g of pyridine were added.

To identify the species responsible for absorbing at 267 nm, small amounts of a cyclohexane solution saturated with HCl were added to a solution of pyridine in cyclohexane. The protonation of pyridine was followed spectroscopically. A species was formed which absorbed at 267 nm and an increase in base line absorbance at all wavelengths is again observed. From this result, it can be concluded that in the titration of $AlCl_2(SG)_n$, at concentrations between 0.3 and 1.6 mmol/g of pyridine, pyridinium chloride is formed from dehydrohalogenation of the catalyst. The dehydrohalogenation of $AlCl_2(SG)_n$ is also the principal reaction leading to loss of activity when the catalyst is used in cracking. As reported previously,[23] addition of HCl to the feed greatly enhances catalyst lifetime for the cracking reactions.

## Conclusions

The calorimetric titrations indicate that the most acidic site on the surface of the $AlCl_2(SG)_n$ catalyst produces a heat of -40 kcal $mol^{-1}$ with pyridine. It has also been shown, using the pyridine/2,6-lutidine comparison, that this was a Brönsted acid site. In addition, Figure 3-5 shows that no significant heat is evolved after the loading of pyridine reaches about 1.5 mmol/g.

It is clear from the infrared titration that the high catalytic activity of the $AlCl_2(SG)_n$ solid acid results from a Brönsted type acid site (initial addition of pyridine produced a spectrum in which the pyridinium ion was the only species present). After the loading of pyridine reaches about 1.3 mmol/g, a second absorbance in the FTIR spectrum starts growing in, indicating that the Brönsted site is fully complexed.

In attempting to use UV/vis spectrophotometry as the method to quantify the amount of pyridine adsorbed by the active catalyst, is was discovered that the pyridinium ion was being produced. When the amount of pyridine added reached 1.6 mmol/g, no more pyridinium ion was formed and free pyridine was found in solution.

In conclusion, the $AlCl_2(SG)_n$ catalyst is a very strong Brönsted acid with about 1.5 mmol/g of active sites and it has been confirmed by the UV/vis adsorption study that the catalyst is deactivated by the loss of HCl.

# CHAPTER 4
# ACIDITY OF PHOSPHOTUNGSTIC ACID

## Introduction

Phosphotungstic acid ($H_3PW_{12}O_{40}$)is a member of the heteropoly acid (HPA) family with a Keggin unit structure (see Figure 4-1). A phosphorus(V) ion occupies the central atom position and is surrounded by a tetrahedron of oxygen atoms. Each of these oxygens is shared by three tungsten(VI) ions and occupies an octahedral position about each tungsten ion. The secondary structure of the bulk solid is illustrated in Figure 4-2. It can be seen here that the Keggin anion exhibits body center cubic packing with the cation being a protonated form of a cluster of water molecules. The number of water molecules depends upon the degree of hydration.

The acidity of heteropoly acids has been investigated by comparing activities of liquid phase[30] and supported[31] HPA to conventional acids in model acid catalyzed reactions. Attempts have also been made to quantify the acidity of HPA using the Hammett acidity indicator method.[32,33] It has been reported that phosphotungstic acid supported on activated carbon is a stronger acid than a sulfonated ion exchange resin[34]. In an attempt to obtain more information about the nature of the acidity of HPA, an in-depth calorimetric and spectroscopic investigation of phosphotungstic acid is reported here.

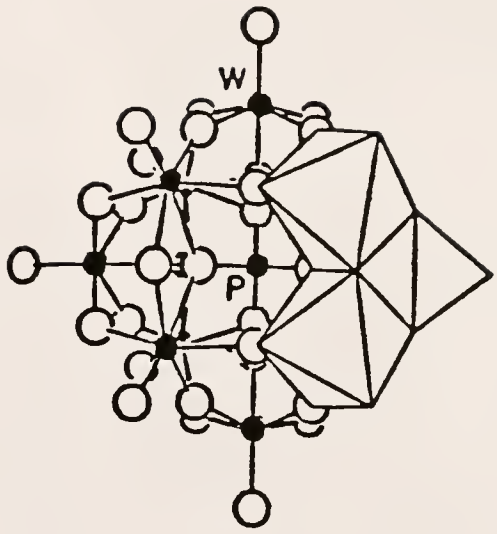



Figure 4-1. Primary structure of phosphotungstic acid.

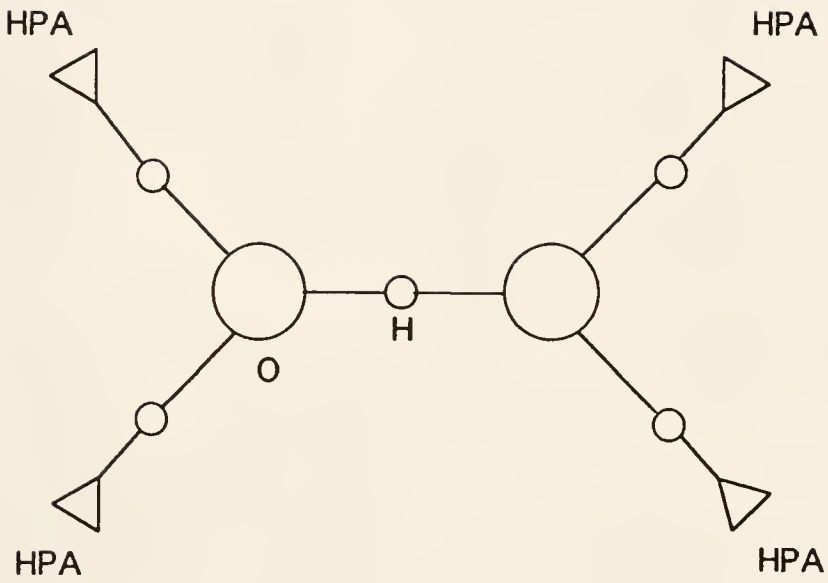



Figure 4-2. Secondary structure of phosphotungstic bulk solid.

Nuclear magnetic resonance (NMR) has been a useful tool for the structural characterization of a large number of different heteropoly acids.[35] Most of this work was directed toward the heteroatoms and addenda nuclei. Attempts to correlate shifts in the NMR due to changes in acidity (as a result of varying hydration conditions) have not been reported. It is not expected that the nuclei mentioned above will undergo significant changes upon loss of water from the structure, but the proton NMR of the HPA in an aprotic solvent may lead to an interesting result.

Calorimetry is an important tool that has not been utilized for the determination of thermodynamic data for phosphotungstic acid. The cal-ad method[12,28] has been designed specifically for the investigation of solid acids/bases. There is a great deal of interest in being able to quantify the acidity of strong acids and in being able to compare the reactivity to other strong acids. By determining enthalpies of interaction of the phosphotungstic acid with a series of bases, E and C values[36] can be calculated for the acid. This then allows for the calculation of an enthalpy of interaction for the acid and any base in the E and C database.

Another important function of calorimetry is its ability to distinguish between Brönsted and Lewis acidity. By comparing the heats evolved using a stericly hindered base (e.g. 2,6-lutidine), coordination to a Lewis acid would be unfavorable and would give less heat than coordination by a slightly weaker base (e.g. pyridine) which has an accessible base site. For a Brönsted base, the sterics would not play a role and the heat for the lutidine would be slightly greater than that for the pyridine.

Infrared spectroscopy is another method which has been used to distinguish between Brönsted and Lewis acid sites. Separate absorbances for the pyridinium ion and Lewis bound pyridine can be found in the 1400-1600 $cm^{-1}$ region of the spectrum[37]. In a photoacoustic-infrared study, the addition of pyridine to phosphotungstic acid resulted in the appearance of exclusively pyridinium ion[38] indicating that this HPA is a Brönsted type acid.

## Experimental

### Purification of Materials

The phosphotungstic acid was obtained from Fisher. It was used as supplied and after various dehydration pretreatments. These pretreatments included evacuation (VAC) and calcination under a flow of $N_2$ (CALC) at different temperatures. The hydrated phosphotungstic acid was white while all heat treated samples of the acid had a faint gray color. The pyridine was distilled over $CaH_2$ using a 12 in. Vigreaux condenser. All other solvents were purified using literature methods[39].

### NMR Spectroscopy

All $^{1}H$ and $^{31}P$ NMR spectra were obtained on a Varian VXR300 300 MHz NMR spectrometer using distilled water or $d_6$-DMSO as the solvent. The proton and phosphorus spectra are referenced to tetramethylsilane (internal standard) and 85% phosphoric acid (external standard) respectively.

Calorimetry

The procedure for the calorimetric titrations has been described in Chapter 1. A volume of either 50 or 75 mL was used in all calorimetric experiments. One gram of phosphotungstic acid was used for a typical titration. Additions of dilute solutions of base to the acid solutions above resulted in final base concentrations ranging from 0.6 to 50 mM.

Fourier Transform Infrared (FTIR) Spectroscopy

All FTIR spectra were obtained on a Nicolet 5PC FTIR spectrometer as Fluorolube or Nujol mulls on NaCl windows and were prepared under a $N_2$ atmosphere.

## Results and Discussion

NMR Spectroscopy

No solvent effect was observed in changing from water to perduetero dimethyl sulfoxide ($d_6$-DMSO) for the $^{31}P$ NMR of the untreated phosphotungstic acid. The chemical shift of the singlet in either solvent was -14.5 ppm (see Figure 4-3). This value is in good agreement with previous reports[35]. The resonance was also insensitive to the drying procedure. From the untreated sample to the most stringent drying condition (evacuation at 250 °C), there was no change in the $^{31}P$ NMR. The fact that this resonance was not affected by the drying procedure is not surprising since the phosphorus is largely removed from the change in the structure (loss of water).

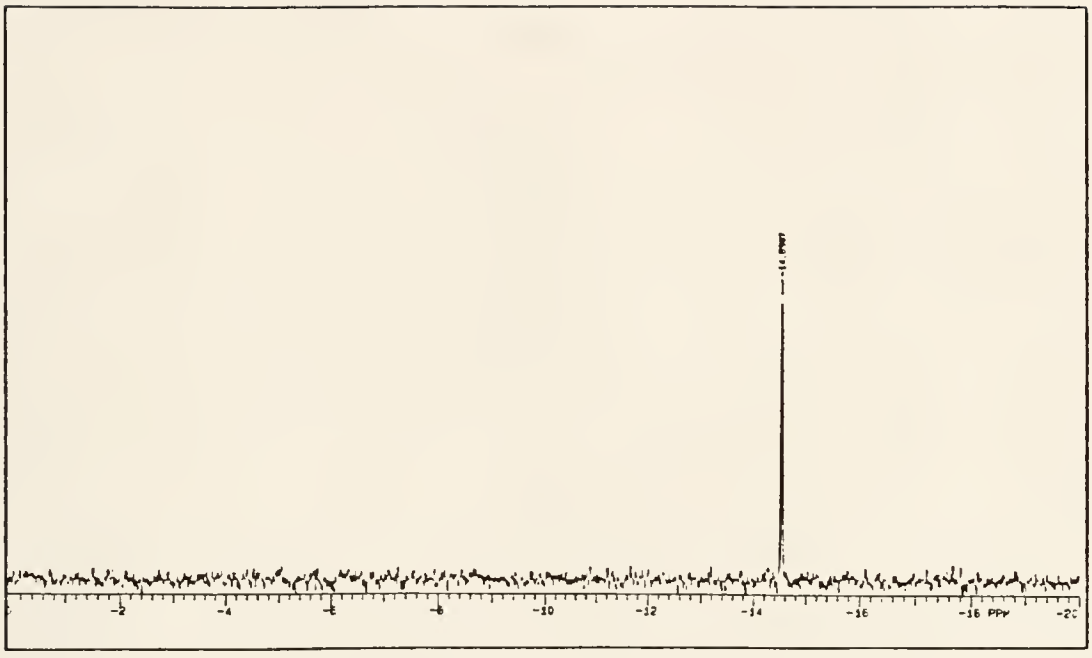



Figure 4-3. $^{31}P$ NMR spectrum of phosphotungstic acid in $H_2O$.

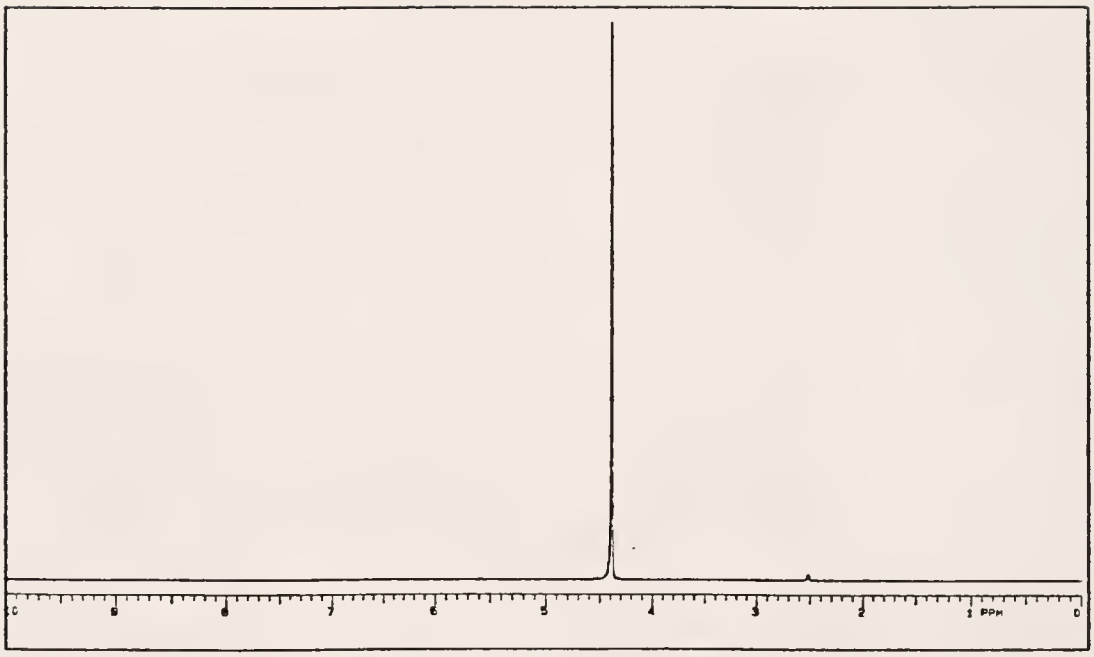



Figure 4-4. $^{1}H$ NMR of untreated phosphotungstic acid in $d_6$-DMSO.

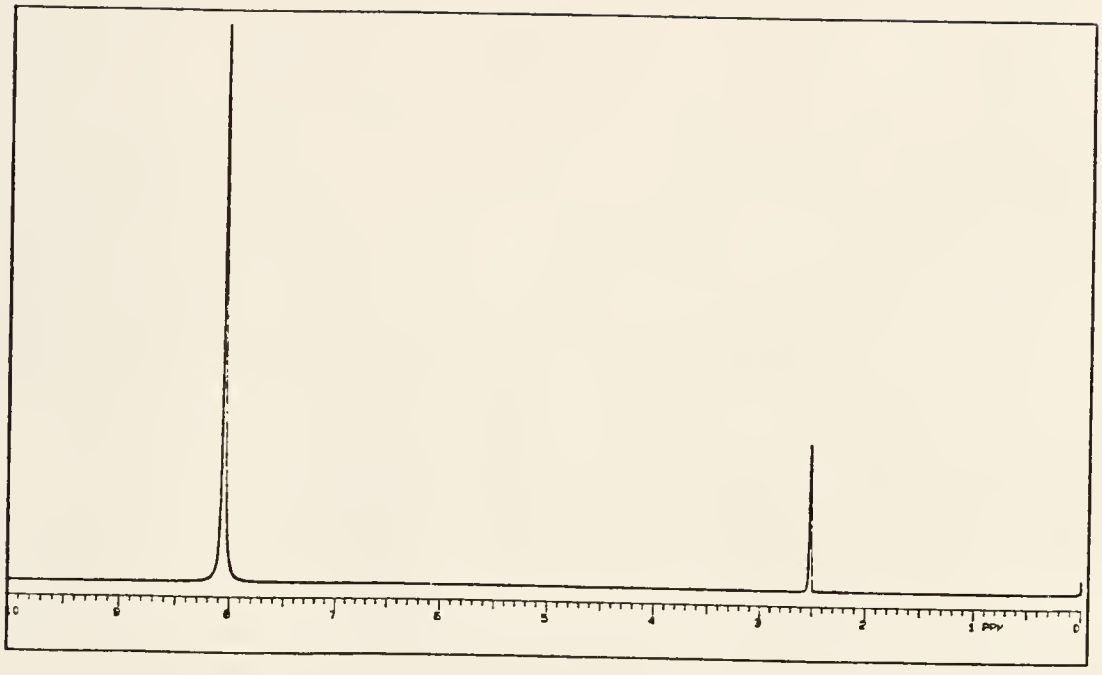


Figure 4-5. $^{1}H$ NMR of phosphotungstic acid calcined at 150 °C in $d_6$-DMSO.

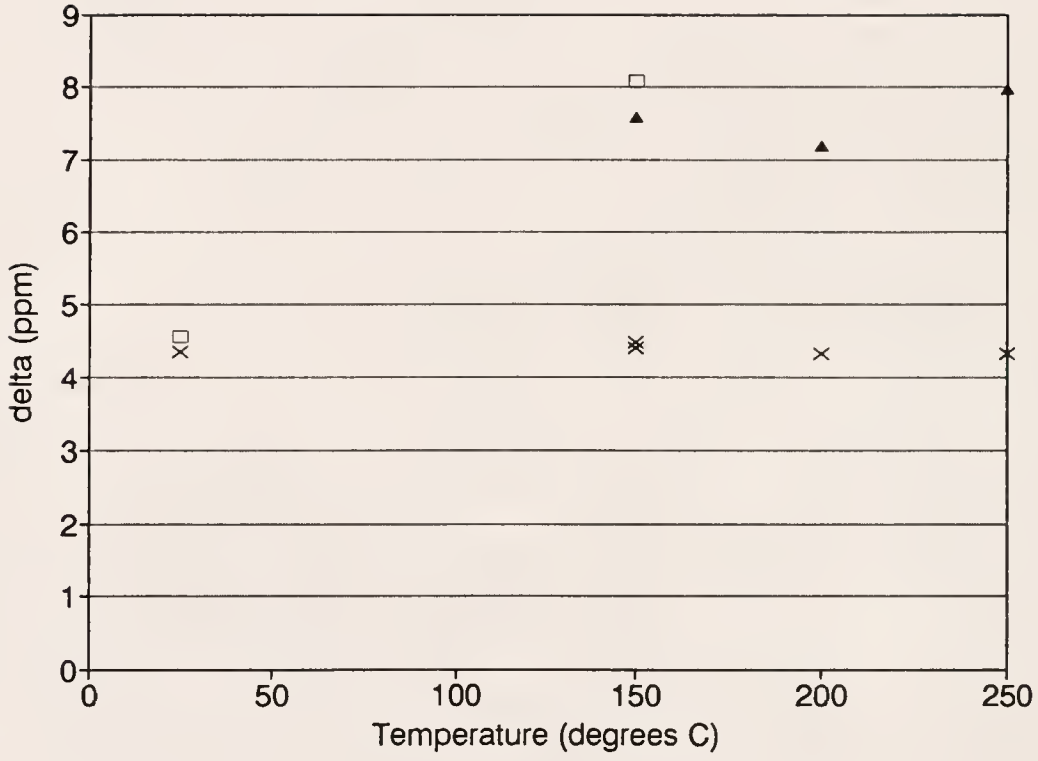



Figure 4-6. $^{1}H$ NMR shift as a function of drying temperature: calcination (□), evacuation (▲), and after addition of water (×).

Since the protons on phosphotungstic acid are acidic, an aprotic solvent ($d_6$-DMSO was chosen) was necessary to observe the $^1H$ NMR of the compound. The untreated acid exhibited a singlet chemical shift of 4.6 ppm (see Figure 4-4). Adding a drop of water to the NMR tube containing the acid in $d_6$-DMSO, the chemical shift was reduced to 4.3 ppm. The $^1H$ NMR of all the dried samples exhibited singlet chemical shifts of 7.8 $\pm$ 0.2 ppm (see Figure 4-5). Upon addition of a drop of water to each of these samples, the chemical shift was reduced to 4.4 $\pm$ 0.2 ppm. Figure 4-6 shows the chemical shifts obtained at different evacuation temperatures. Even though this physical method reveals a change in the structure with a change in the pretreatment, it is not a good measure of acidity since the spectral change is not proportional to the change in acidity, *vide infra*.

Calorimetry

The initial titrations were conducted on a 25 w/w% phosphotungstic acid on Ambersorb® 572 carbon molecular sieve. Due to difficulties in obtaining heats from the bead form of the support[40], the doped carbons were powdered. To determine the solid acidity of the supported acid, the cal-ad method was used. This method requires the use of a poorly solvating solvent in order to eliminate enthalpic contributions due to dispersion interactions. When a pyridine titration was conducted in cyclohexane, there was no noticeable difference in the heat evolved between the undoped and doped supports.

In a further attempt to determine the solid acidity of the phosphotungstic acid, a similar pyridine titration was conducted on the bulk solid in cyclohexane. There was no detectable heat evolved but an infrared spectrum of the solid after the titration provided a promising result, *vide infra*.

The difficulty in obtaining any heat from the solid arises from its low surface area (surface area for the phosphotungstic acid is generally found to be less than 10 $m^2 g^{-1}$). It has been reported[31,41] that the heteropoly acids display "pseudo liquid phase" behavior with respect to polar solvents. That is, the presence of some polar solvent molecules allow transport into the bulk of the solid. This allows access to sites which are not on the external surface of the bulk solid.

Acetonitrile was then chosen as the solvent for the calorimetric titrations (it should be noted that the phosphotungstic acid, with no pretreatment, was soluble in acetonitrile). It is polar and weakly basic, so the heat evolved for the addition of a stronger base will include the displacement of the acetonitrile from the acid site as well as enthalpy for the coordination of the stronger base to that site. When pyridine was used as the titrant, a significant amount of heat was observed (see Figure 4-7). A calculation of the enthalpy of interaction for each injection, assuming complete complexation of the pyridine, gives rise to an interesting result. Figure 4-8 shows the graph of calculated enthalpies as a function of total moles of pyridine added. This graph shows that a constant enthalpy ($-6.8 \pm 0.3$ kcal $mol^{-1}$) is obtained for this titration and heat is evolved until the amount of pyridine reaches about one mmol. This corresponds to three times the number of

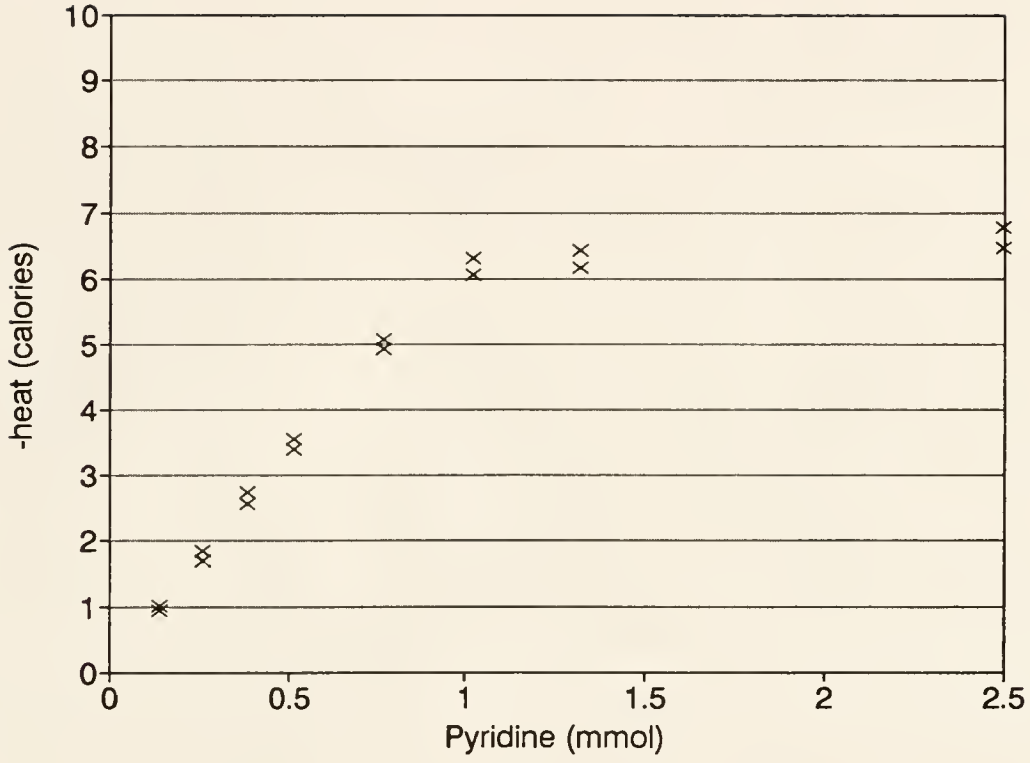



Figure 4-7. Heat evolved as a function of pyridine added in acetonitrile.

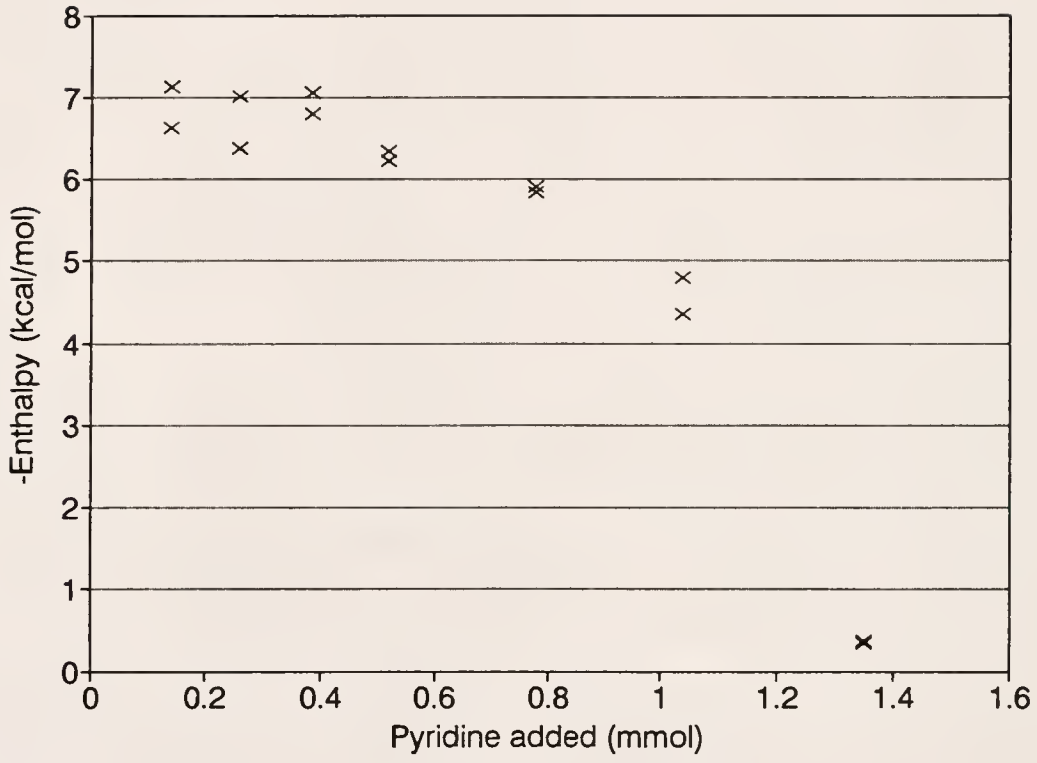



Figure 4-8. Enthalpies calculated assuming complete complexation of pyridine.

moles of phosphotungstic acid in solution which suggests all three protons of the acid have been completely complexed.

In an attempt to determine how the acidity of the phosphotungstic acid is affected by dehydration, several samples were prepared under various drying conditions. Figure 4-9 and Figure 4-10 illustrate the effects of evacuation and calcination at various temperatures respectively. It is interesting to note that all the dehydrated samples were only slightly soluble in acetonitrile but the endpoint of each titration continued to occur at the same place as in the hydrated sample (about one mmol of base added). None of the enthalpies obtained from all of the samples that were dried under vacuum remained constant although it is interesting that the samples evacuated at 150 °C and 200 °C had a similar site distribution but the sample evacuated at 250 °C contained much stronger sites. The decrease in enthalpy with each injection suggests that the conversion of the weaker to stronger acid sites is not complete and the enthalpies calculated are an average of the strong and weak sites. Calcination at elevated temperatures seemed to convert all the acid sites to the same type of site, but the acidity of that site was dependent upon the amount of time the sample was exposed to the elevated temperature. Figure 4-10 shows that an enthalpy of 17.4 $\pm$ 0.4 kcal $mol^{-1}$ is obtained when the acid is calcined at 300 °C for three hours and an enthalpy of 31.4 $\pm$ 0.9 kcal $mol^{-1}$ is obtained after twelve hours at 300 °C.

It is important to determine if the dehydration procedure changes the nature of the acidic site. To determine if the Brönsted sites were converted to Lewis sites, titrations of the dried samples were conducted using 2,6-lutidine to discriminate between the two

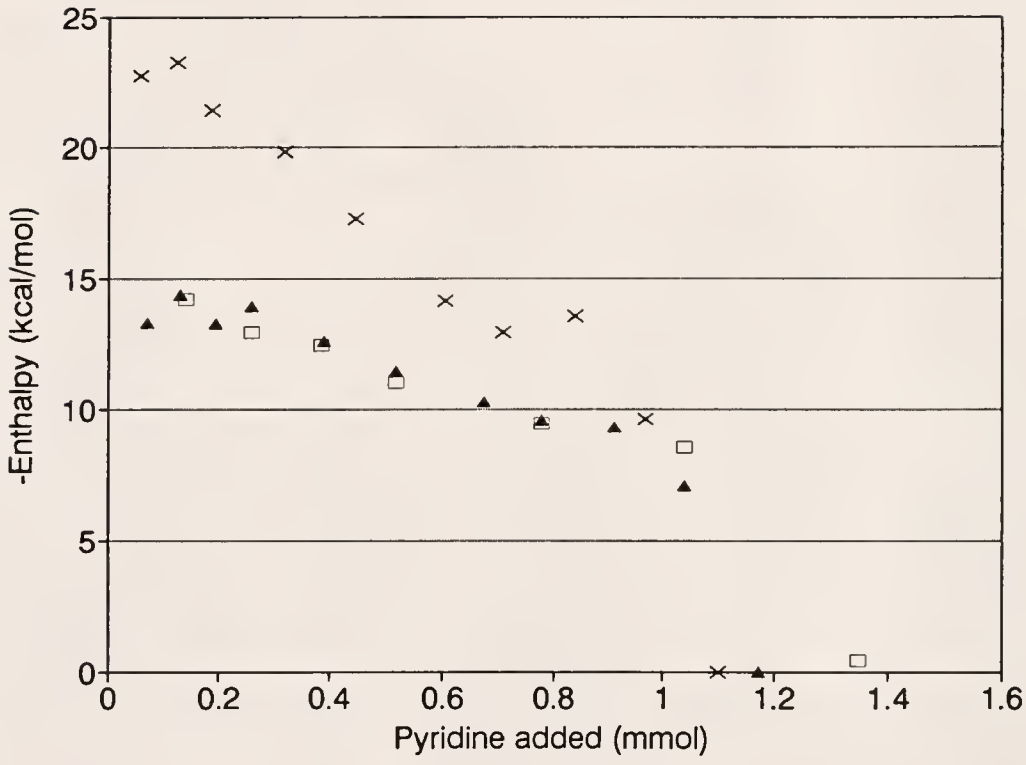



Figure 4-9. Calculated enthalpies for each addition of pyridine on phosphotungstic acid samples evacuated at 150 °C (□), 200 °C (▲), and 250 °C (×).

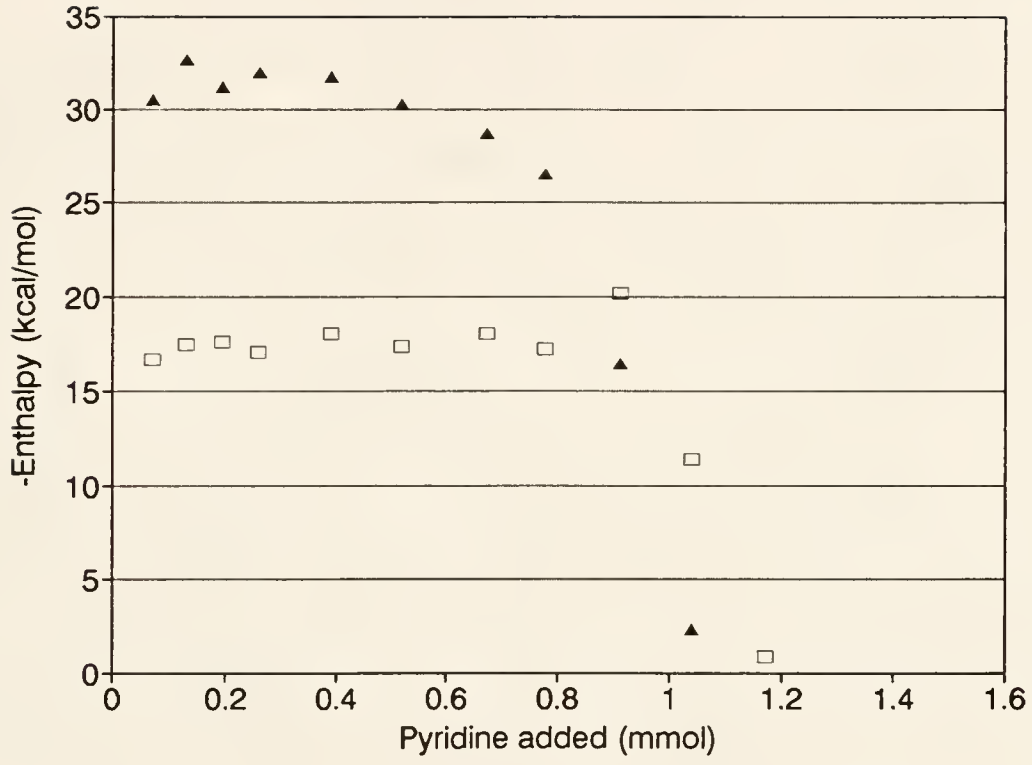



Figure 4-10. Calculated enthalpies for each addition of pyridine on phosphotungstic acid samples calcined at 300 °C for 3 hours (□) and 12 hours (▲).

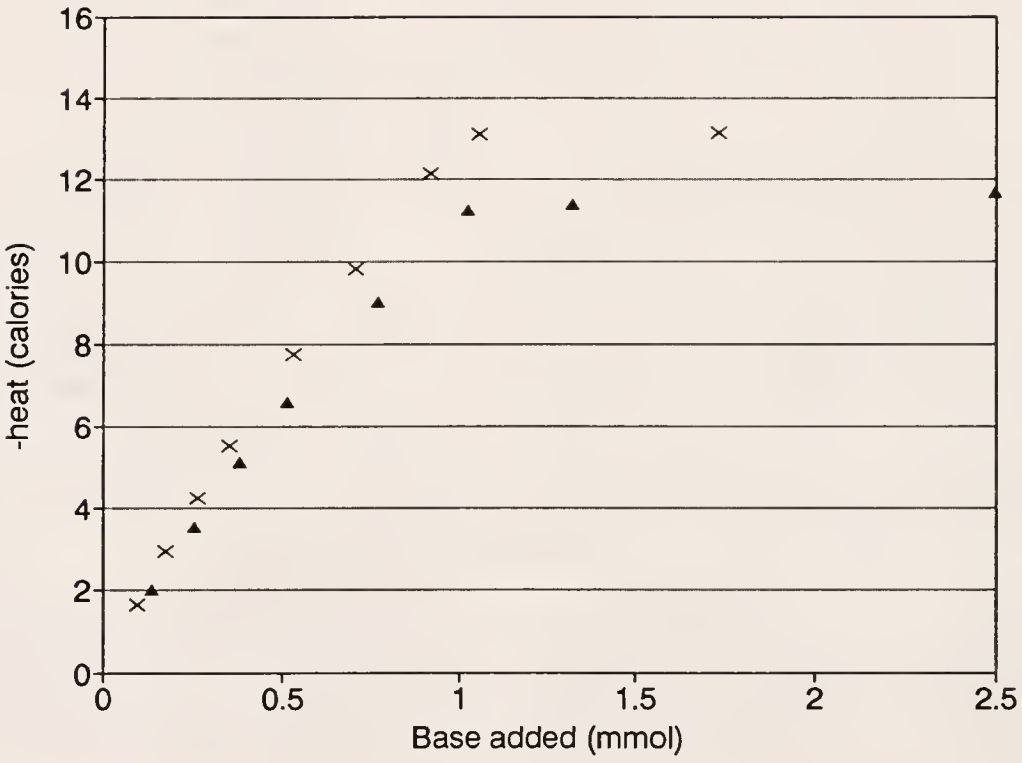



Figure 4-11. Heats evolved for titration of phosphotungstic acid evacuated at 150 °C with pyridine (▲) and 2,6-lutidine (×).

as described in Chapter 3. Figure 4-11 illustrates the results of these titrations. The heats obtained for the additions of 2,6-lutidine to the dried phosphotungstic acid yielded heats slightly higher than those obtained for pyridine at the same concentration. This indicates that the drying procedure merely enhances the Brönsted acidity and does not convert the Brönsted sites to Lewis sites.

FTIR Spectroscopy

The FTIR spectrum of the bulk phosphotungstic acid after the initial titration in cyclohexane (which did not yield any detectable heat) is shown in Figure 4-12. This spectrum shows the presence of pyridinium ion (absorbance at 1540 $cm^{-1}$) indicating that there are sites on the acid which are strong enough to be completely ionized. It is apparent from this and the calorimetry data that there are strong acid sites present in the phosphotungstic acid but a majority of them are not accessible in the non-polar cyclohexane. Infrared spectra taken of the phosphotungstic acid samples recovered at the conclusion of the calorimetric titrations in acetonitrile also contained the same bands indicating Brönsted acidity.

## Conclusions

The acidity of the phosphotungstic acid has been shown to be of a Brönsted nature. Upon dehydration of the acid, the sites become stronger acids. The conversion of the sites is dependent upon the method and length of pretreatment. When the acid is vacuum dried, there are different strength sites present giving rise to calorimetry data

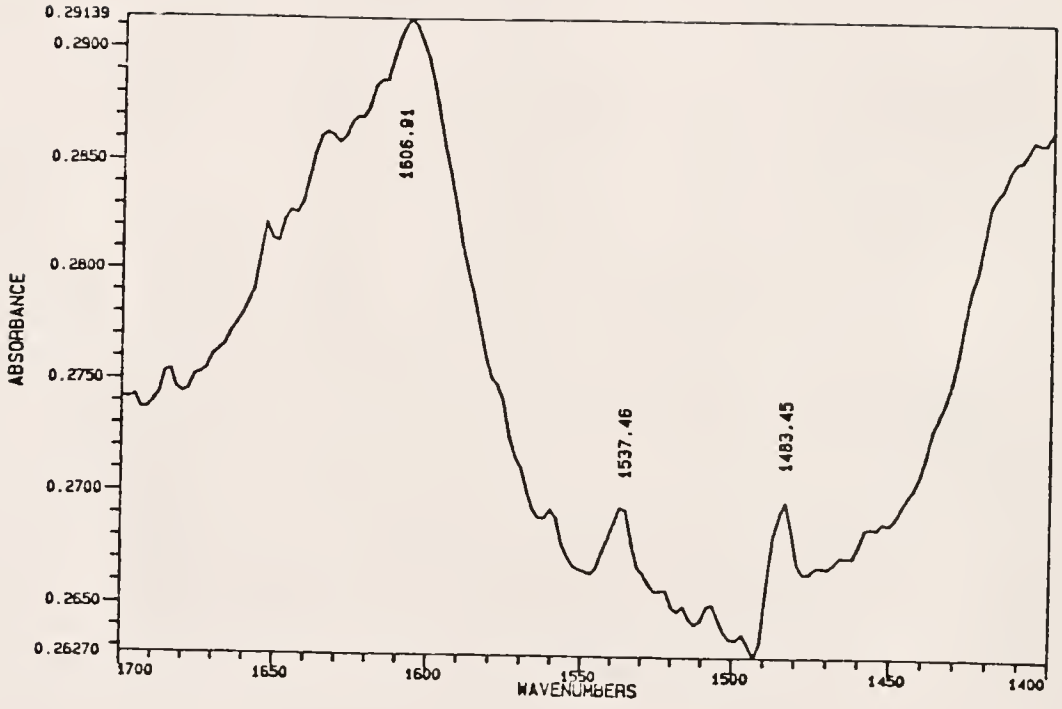



Figure 4-12. Fluorolube mull spectrum of phosphotungstic acid after pyridine.

which averages the strengths of the sites. Calcination of the acid converts all the sites to the same strength and longer calcination times at the same temperature yield stronger sites. The "pseudo liquid phase" behavior reported previously[31,41] for the heteropoly acids has also been confirmed here. The calorimetric experiments in cyclohexane didn't yield measurable heats because of the small number of sites accessible, but the strong sites were found to be present in the FTIR spectrum. When acetonitrile was used as the solvent, its polarity allowed access to all the sites of the acid.

# CHAPTER 5
# ACIDITY OF HY ZEOLITE

## Introduction

Research in the field of zeolites encompasses a very large range of materials and applications. Novel zeolites are continually being synthesized for a great variety of chemical needs (a number of these have been reviewed by Davis[42]). The basic structure of a zeolite consists of a framework of neutral silicon dioxide moieties covalently linked to negatively charged aluminum(III) moieties[43] (see Figure 5-1). This creates a negatively charged framework and requires a cation to maintain charge balance. The ability of the zeolite to act as a cation exchanger is one of the properties responsible for its popularity. The amount of counter ion needed to balance the framework charge can be tailored by incorporating the desired amount of aluminum dioxide moieties. Another reason for the zeolites popularity arises from the fact that the framework is porous. This porosity is another variable which can be synthetically tailored. A good example of this is the shape selective catalytic isomerization of hydrocarbons using the channel-like structure of H-ZSM-5.

Out of this vast array of zeolites, HY was chosen as the first to be studied using the novel cal-ad method because the acid form of this zeolite has been of interest in acid catalyzed reactions in industry. There has been a great deal of work reported on the

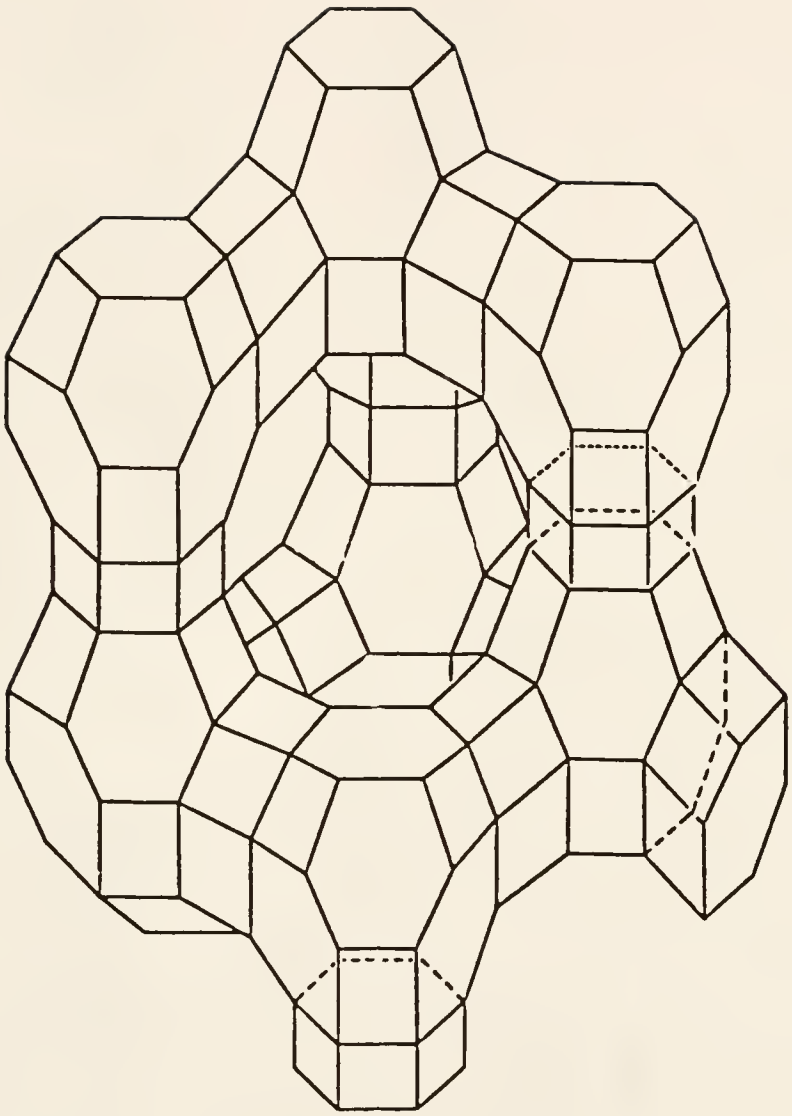


Figure 5-1. Structure of Y Zeolite.

structural characterization of Y zeolites[43] including an X-ray crystal structure[44] and a pulsed-neutron powder diffraction[45] as well as many methods for the determination of the acidity of the acid form.

A physical method that has been utilized extensively is infrared spectroscopy. Early work in this area included investigations of the hydroxyl region to distinguish between different types of hydroxyls on the surface.[46,47] The results of these studies concluded that there are three bands in the hydroxyl region. A band at 3742 $cm^{-1}$ results from absorbance by isolated silanols (similar to those found in silica). Two bands present at 3643 $cm^{-1}$ and 3540 $cm^{-1}$ result from absorbance by bridging hydroxyls in the large cage ($\alpha$-cage) and small cage ($\beta$-cage) respectively. Many of these studies also included adsorption of bases (ranging from ethylene to water) from the gas phase to determine the effect of coordination on the infrared spectrum.

Another method which has received a great deal of attention more recently is nuclear magnetic resonance. Although the aluminum and silicon centers are active NMR nuclei, they have not been very useful for the determination of the acidity of zeolites. The most informative work has involved $^{1}H$ NMR. Resonances corresponding to the same hydroxyl species described above have been separated and assigned.[48] The use of basic probes with NMR active nuclei has also been an area of increasing interest. A great deal has been done with nitrogen[49] and phosphorus[50] NMR studies but they have not led to a direct quantification of the zeolites acidity.

Other methods that have been used (temperature programmed desorption[51] and a gas chromatographic technique[52]) have met with limited success. There have also

been microcalorimetric investigations into the acidity of HY.[53] These have studies involved the gas phase adsorption of pyridine or ammonia and concluded that there is a uniform distribution of strong acid sites with heats of adsorption of 113-125 kJ/mol for ammonia. It is interesting to note that other zeolite samples (e.g. H-ZSM-5) examined in these studies did not contain a uniform distribution of strong acid sites, but did exhibit slightly higher heats of adsorption.

Another important aspect of the acidic zeolite is its ability to convert its Brönsted acidity to Lewis acidity. It has been well established that this can be accomplished by calcination of the zeolite at temperatures above 500 °C.[47] It is also well established[54] that the mechanism for this conversion consists of the release of aluminum from the framework concomitant with dehydroxylation creating an extraframework aluminum hydroxide species. This species is further dehydroxylated to yield a coordinatively unsaturated $Al^{3+}$ Lewis acid center.

In this study, the cal-ad method was used on the HY zeolite in an attempt to distinguish the different acid sites calorimetrically. Concurrently, FTIR spectroscopy was used in addition to the calorimetric results. These results were also correlated using the E and C analysis[13] to determine if the interactions of the bases with the solid acid could be predicted using the solution data for the bases currently available in the E and C database.

## Experimental

### Purification of Materials

The Y zeolite was obtained from Aldrich in the ammonium exchanged form (molecular sieves catalyst support, Linde LZ-Y62, Lot # 00220BZ). This was converted to the acid form by calcination under flowing $N_2$ for 24 hours at either 350 °C (HY350) or 650 °C (HY650). The cyclohexane was filtered three times over activated carbon followed by distillation over $P_2O_5$. The pyridine was distilled over $CaH_2$ using a 12 in. Vigreaux column. All other solvents were purified using literature methods[39].

### Calorimetry

The procedure for the calorimetric titrations has been described in Chapter 1. A volume of 50 mL and a mass of 0.5 g of zeolite were used in all calorimetric experiments. Additions of dilute solutions of base to the slurries above resulted in final base concentrations ranging from 0.8 to 50 mM.

### Fourier Transform Infrared (FTIR) Spectroscopy

All FTIR spectra were obtained on a Nicolet 5PC FTIR spectrometer as Fluorolube on NaCl windows and were prepared under a $N_2$ atmosphere. The infrared titrations were done in 10 mL of $CCl_4$ on 0.1 g of zeolite. The zeolite was handled under an inert atmosphere at all times.

## Results and Discussion

### Calorimetry

A non-polar solvent (cyclohexane) was chosen for the calorimetric titrations in order to obtain an enthalpy of interaction, between the solid acid and the base probe molecule, in which the dispersion interactions are cancelled out. Figure 5-2 shows the results of several titrations of HY350 with pyridine. There was some difficulty in obtaining results that were as reproducible as the previous calorimetric results. This may be attributed to the zeolites great affinity for water. The difficulty may also arise from a difficulty in diffusing to the interior sites of the zeolite on a reasonable timescale for the calorimetric experiment (in almost every case, higher concentration injections yielded broader deflections than at lower concentrations, indicating heat evolution over a longer time frame). In order to use the cal-ad method, the adsorption data for the HY350 samples were then obtained. For every addition of pyridine, up to 1.32 mmol $g^{-1}$, the zeolite sample completely adsorbed the probe. This result leads to one of two conclusions. The first is that the number of acid sites in the zeolite is larger than the amount of pyridine that has been added (for the formula $H_{56}[(AlO_2)_{56}(SiO_2)136)]$, the maximum number of protonic sites would be 0.49 mmol/g). If this is the case, the equilibrium constant for coordination to these sites would have to be very large so that complete complexation of the base was occurring. The second possible conclusion is that physisorption of the base is facilitated by the porous structure of the zeolite which concentrates the pyridine in the pores of the zeolite and leaves none in the bulk solution.

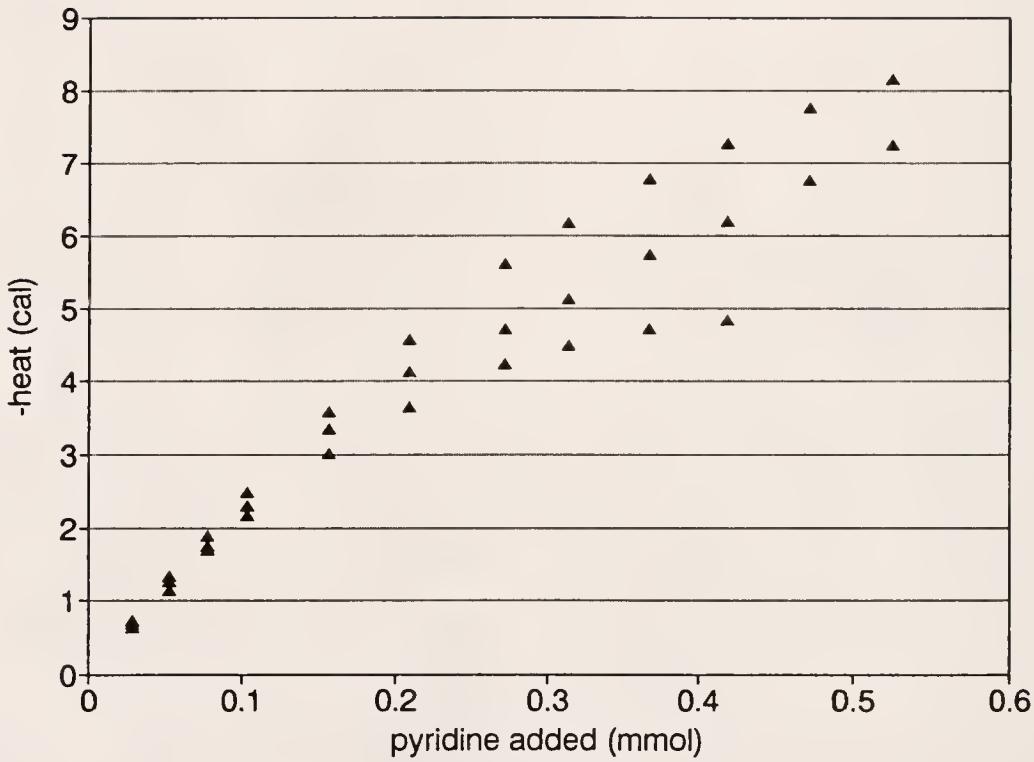



Figure 5-2. Heats evolved for titrations of HY350 with pyridine.

The difficulty with either of these interpretations is that the base concentration in solution cannot be measured over the range in concentration used for the calorimetric experiments. This makes it impossible to determine a value for the equilibrium constant of binding for the cal-ad analysis.

Since the adsorption data are not helpful in the determination of the zeolites surface thermodynamics, a strictly calorimetric approach has been taken. This approach is susceptible to the same scrutinies as previous calorimetric investigations of solids were as described in Chapter 1. Figure 5-3 illustrates the calculated enthalpies for each addition of pyridine assuming complete complexation of the base on HY350. This graph shows an initial enthalpy of -24.0 $\pm$ 1.9 kcal $mol^{-1}$ up to 0.05 mmol of pyridine added. From 0.05 to 0.12 mmol of pyridine a constant enthalpy of -20.4 $\pm$ 1.8 kcal $mol^{-1}$ is obtained. Between 0.12 and 0.3 mmol of pyridine added, there is a decrease in the enthalpy calculated for each addition. This is caused by the transition from the strong sites to the much weaker sites. The calculated enthalpies in this range are the mole fraction average of the few strong sites still remaining along with the abundance of weak sites. From 0.3 to 0.52 mmol of pyridine added a third enthalpy of -9.3 $\pm$ 2.4 kcal $mol^{-1}$ is calculated. Even though the enthalpy calculated for the first two sites have overlapping error limits, it appears more clearly in Figure 5-3 that they are two distinct sites.

Since the mass of zeolite for the calorimetric titrations was 0.5 g, the theoretical maximum number of strong protonic sites corresponds to 0.245 mmol of pyridine added. This corresponds to the region in Figure 5-3 in which there is an averaging of strong and

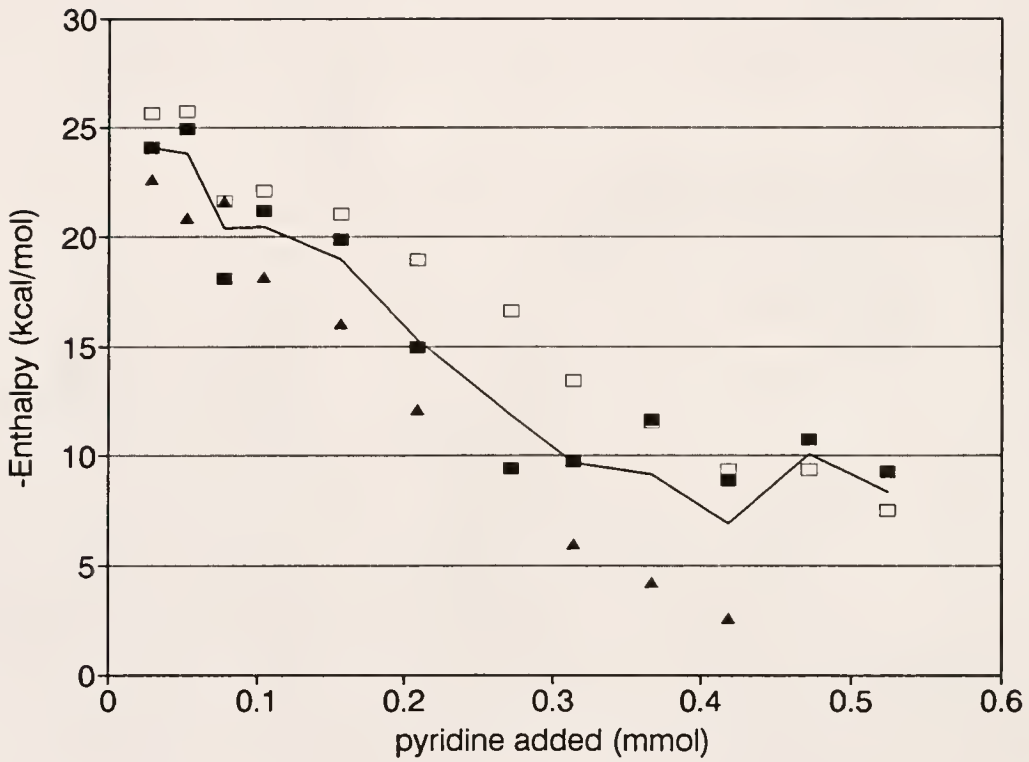



Figure 5-3. Enthalpies for pyridine addition on HY350, assuming complete complexation of pyridine. The line corresponds to the average of the three experimental points at each concentration.

weak sites. The weak sites in the zeolite may be due to remaining silanol functionality (note in Chapter 2 that at a calcination temperature of 450 °C for silica there were still isolated silanols remaining).

A comparison of the heats evolved for pyridine and 2,6-lutidine is given in Figure 5-4. The first addition of 2,6-lutidine yields an enthalpy of -26.4 kcal $mol^{-1}$ but it is obvious that the number of sites accessible to this base are greatly reduced compared to those accessible to pyridine. In this case this reduced number of sites is not the result of Lewis acidity, *vide infra*, but is due to the small pore openings (7.1 Å opening into $\alpha$-cage[43]). The distance across the methyl groups of the 2,6-lutidine molecule is 6.99 Å. This denies accessibility of the probe to the internal pore structure. The conclusion from this is that the number of sites on the external surface (surface accessible from the bulk solution) of the zeolite is slightly less than 0.1 mmol $g^{-1}$ (since the first addition of 2,6-lutidine was 0.049 mmol onto a 0.5 g sample of HY350).

The heats obtained for the calorimetric titration of HY650 using pyridine as the probe are shown in Figure 5-5. A constant enthalpy was not obtained at any point throughout the entire concentration range. All the heats were less than those obtained for HY350 indicating that the Lewis sites that are produced by this calcination procedure are slightly less acidic than the corresponding Brönsted site.

FTIR Spectroscopy

The 1400-1700 $cm^{-1}$ region of the infrared spectrum has been used extensively[47,4] for the differentiation of acid site types (i.e. Brönsted or Lewis). The typical absorbance

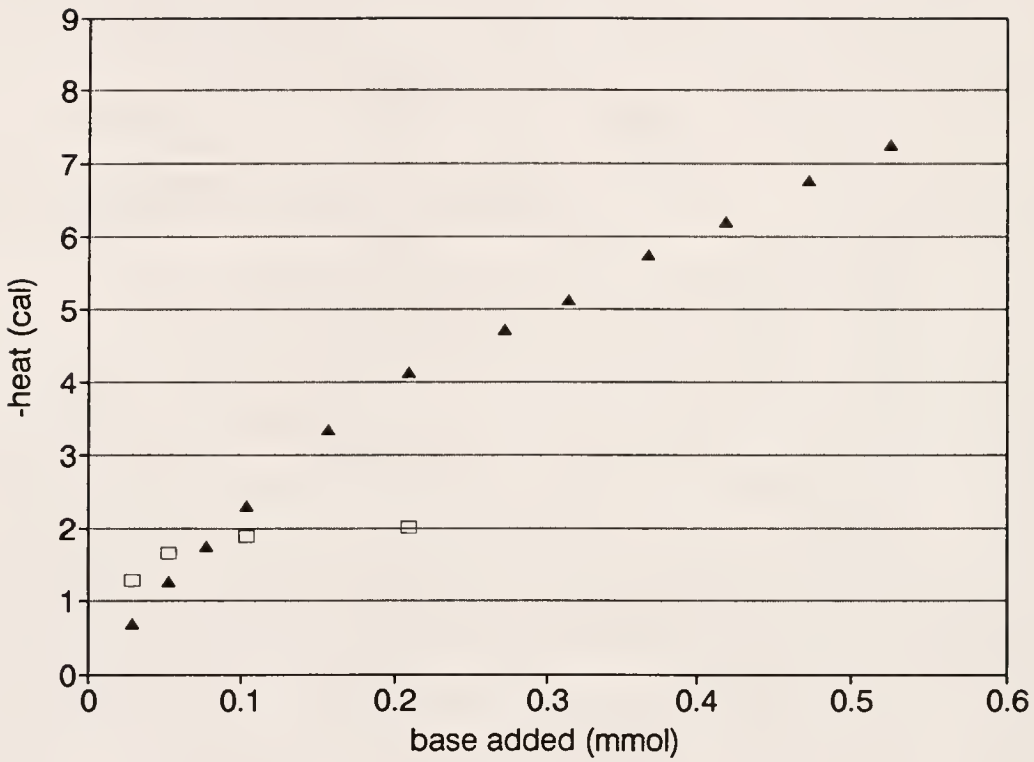



Figure 5-4. Comparison of calorimetric titrations of HY350 with pyridine (▲) and 2,6-lutidine (□).

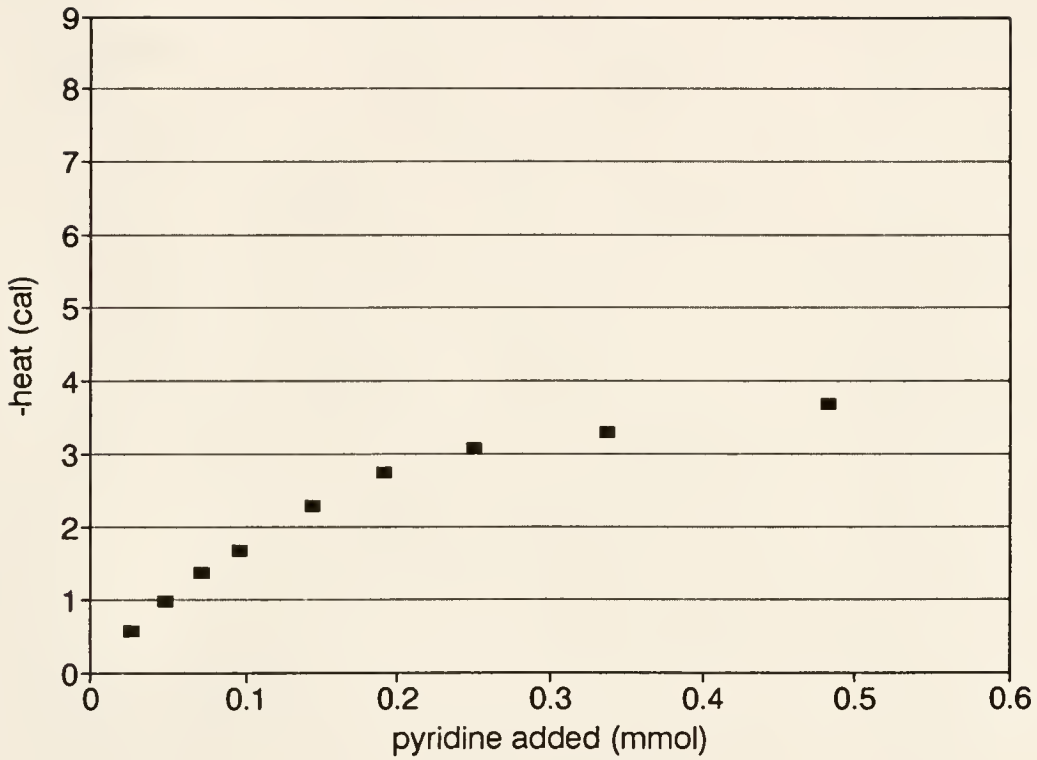



Figure 5-5. Heats obtained for titration of HY650 with pyridine.

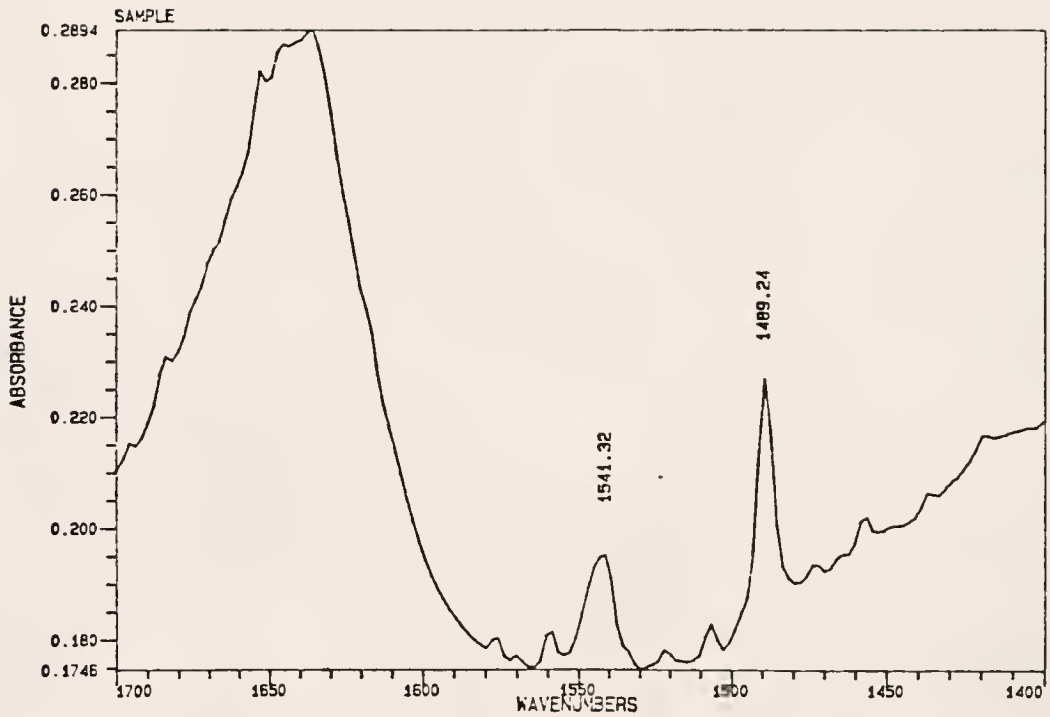



Figure 5-6. FTIR spectrum of HY350 after pyridine adsorption from $CCl_4$ followed by evacuation at 25 °C (Fluorolube mull).

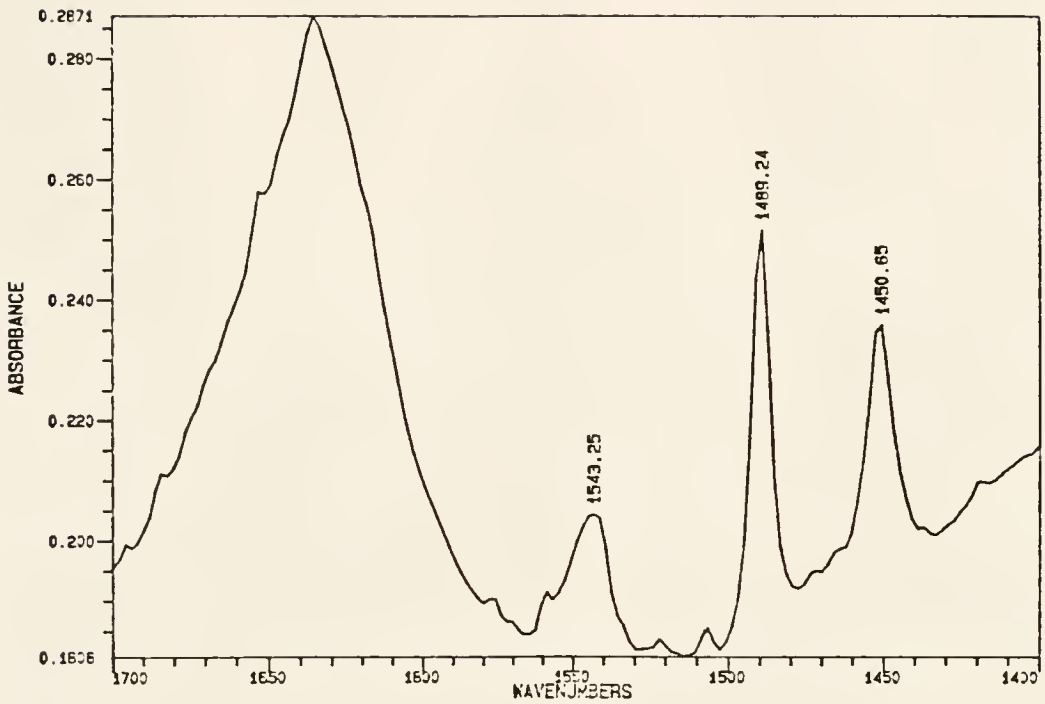



Figure 5-7. FTIR spectrum of HY650 after pyridine adsorption from $CCl_4$ followed by evacuation at 25 °C (Fluorolube mull).

for the pyridinium ion (Brönsted site) occurs around 1540 $cm^{-1}$ while the Lewis site absorbance can be found between 1440 and 1455 $cm^{-1}$. Figure 5-6 shows the presence of exclusively Brönsted acidity on HY350 whereas Figure 5-7 illustrates the Lewis acidity of HY650.

Infrared spectra for the pre-calcined ($NH_4Y$), HY350, and HY650 zeolites are shown in Figure 5-8. It is easy to see, from these spectra, the loss of ammonia in going from $NH_4Y$ to HY350. The loss of acidic hydroxyls is also apparent from the comparison of the HY350 and HY650 spectra. The spectrum of HY350 is curious in that there appears to be only one absorbance in the acidic hydroxyl region. This is contrary to all previous reports[43,46,47] for this type of zeolite. The reason for this is the technique in which the spectra were obtained. In the previous reports, all the spectra were taken as self-supporting pellets of the zeolite, whereas here the spectra are taken as Fluorolube mulls of the zeolite. The peak position of the single absorbance in the Fluorolube mull is nearly in the middle (3588 $cm^{-1}$) of the two absorbances previously reported (3643 and 3540 $cm^{-1}$). It appears from this that the presence of Fluorolube broadens these bands to the point that they are no longer separable.

An infrared titration of HY350 with pyridine is shown in Figure 5-9. The asymmetry of the hydroxyl peak becomes more apparent after the addition of pyridine indicating the presence of the two different hydroxyl absorbances. Another point that is interesting is that instead of a shift in the O-H stretch, as would be expected upon coordination, it seems as though the proton has been completely removed from the oxygen. This should not be surprising since it has already been shown that the

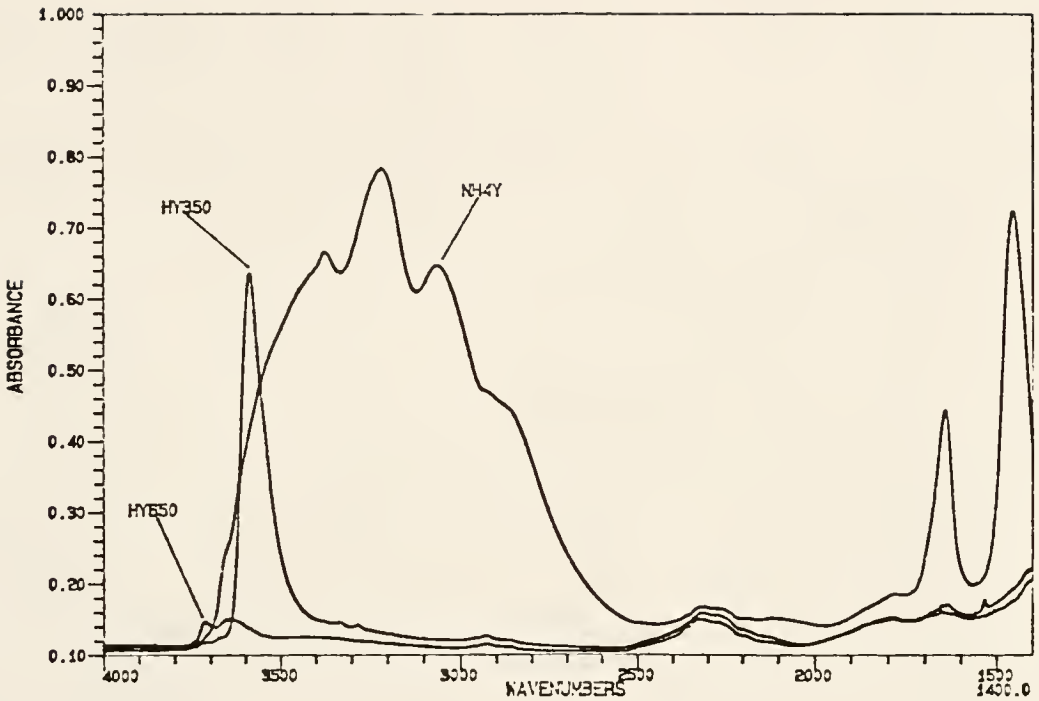



Figure 5-8. FTIR spectra of $NH_4Y$, HY350, and HY650 as Fluorolube mulls.

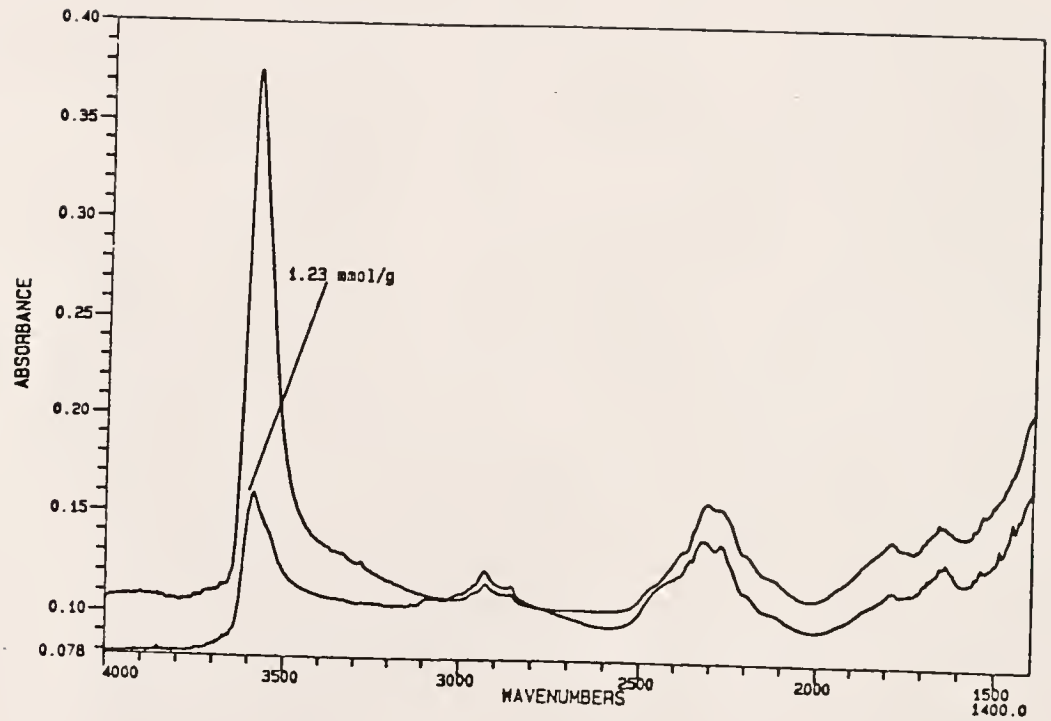



Figure 5-9. FTIR titration of HY350 with pyridine (Fluorolube mull).

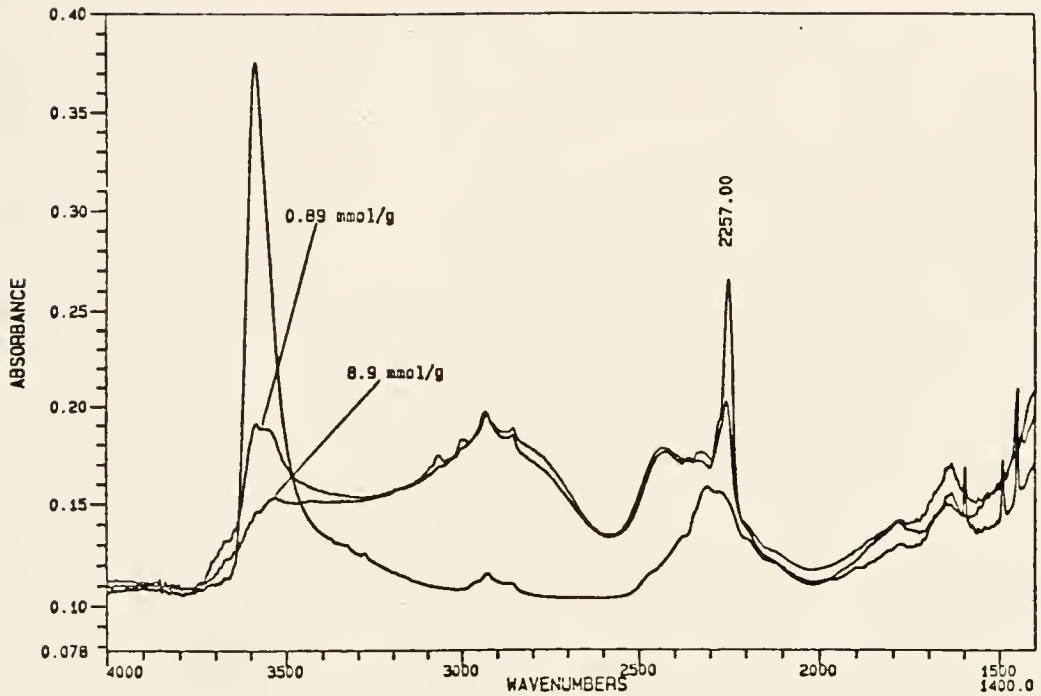



Figure 5-10. FTIR titration of HY350 with benzonitrile (Fluorolube mull).

pyridinium ion is formed in this reaction. In order to see a shift in the O-H stretching frequency, an infrared titration of HY350 with benzonitrile was performed (see Figure 5-10). Again the asymmetric nature of the hydroxyl absorbance becomes more apparent with the addition of base. In this case, the O-H stretching frequency shift can be observed (about 700 $cm^{-1}$). The shift in the cyanide stretch can also be seen (from 2232 $cm^{-1}$ for neat benzonitrile to about 2425 $cm^{-1}$). The absorbance at 2257 $cm^{-1}$ is assigned to physisorbed benzonitrile as this absorbance is removed upon evacuation at 25 °C.

E and C Analysis

A determination of the acidity of HY zeolite can be obtained by determining heats of interactions from calorimetric data for the interaction of a series of bases with the zeolite. The E and C model[13] (see Equation 2-2) has been used to interpret enthalpies if interaction for large database of acids and bases. By substituting the enthalpies obtained for the low concentration additions of each base and the reported[13c] $E_B$ and $C_B$ values for each respective base into Equation 2-2, a series of equations is obtained. These equations are then solved simultaneously for the best $E_A$ and $C_A$ for the zeolite. The $E_A$ and $C_A$ values obtained for the strongest site on HY350 are 7.15 $\pm$ 0.96 (kcal $mol^{-1})^{0.5}$ and 2.74 $\pm$ 0.52 (kcal $mol^{-1})^{0.5}$ respectively. The data fit is shown in Table 5-1. A good fit results indicating that the enthalpies of adsorption for these donors by HY350 are dominated by donor-acceptor interactions. The $E_A$ and $C_A$ values obtained here for HY350 can now be used to predict the enthalpies of interaction for more than 70 other

Table 5-1 Results of E and C fit for the most acidic site on HY350.

| | Base[a] | $-\Delta H_{exp}$ (kcal/mol) | $-\Delta H_{calc}$ (kcal/mol) | Deviation (kcal/mol) |
|---|---|---|---|---|
| 34 | Benzonitrile | 13.6 | 13.9 | 0.3 |
| 79 | THTP[b] | 12.0 | 13.0 | 1.0 |
| 49 | DMA[b] | 19.5 | 20.4 | 0.9 |
| 16 | Pyridine | 24.0 | 22.4 | 1.6 |

[a] Numbers to the left of the base indicate their call number in the E and C database.[13c]

[b] THTP is tetrahydrothiophene and DMA is N,N-dimethylacetamide

donors in the E and C database.[13c] This information can be extremely useful in further research into possible applications of this zeolite.

## Conclusions

The previously reported[43,47] effects of heat treatment on $NH_4Y$ to produce HY have been reproduced. Calcination of the ammonium form of the zeolite at 350 °C produces a zeolite with Brönsted acidity and calcination at 650 °C produces a zeolite with Lewis acidity. Determination of the acidity of HY350 was accomplished by calorimetric titration of HY350 with pyridine. The data from these titrations indicated the presence of two strong acid sites with very similar strength and a weak acid site. By titrating HY350 with a series of bases, the values $E_A = 7.15$ and $C_A = 2.74$ were obtained for the strongest acid site. These values allow the prediction of a large number of enthalpies. More importantly, they provide the ability to determine when interactions with this zeolite do not follow simple donor-acceptor trends in reactivity.

# CHAPTER 6
# SUMMARY

A novel calorimetric-adsorption (cal-ad) method has been developed to facilitate the determination of surface acidity/basicity. By combining a calorimetric determination of the heats evolved and a spectroscopic determination of probe adsorbed for consecutive additions of probe to a slurry of solid acid, the surface thermodynamics of the solid can be determined. This includes the number of different types of sites as well as the quantity, equilibrium constant of binding, and enthalpy of binding of each of these different sites.

Application of this method to silica gel revealed three different types of hydrogen bonding sites. FTIR spectroscopy was used to confirm the presence of these different sites. Values of $E_A = 2.30$ and $C_A = 2.48$ for the most acidic site on silica were also calculated. Work that is continuing in the Drago group includes an a calorimetric investigation of other bases with this strongest site to achieve a better determination of the above values.

The first fundamental difficulty in the use of the cal-ad method was encountered when the $AlCl_2(SG)_n$ catalyst was studied. Although this was the strongest acid studied ($-\Delta H = 40$ kcal $mol^{-1}$ pyridine added) studied, the cal-ad method could not be used. The equilibrium constant of binding was so large that the amount of pyridine remaining in solution was below the detection limit of the UV/vis spectrophotometer. A requirement

for the mathematical application of the cal-ad method is that the probe concentration remaining in solution must be measurable in the same concentration range in which the calorimetric titration yields heat. Since the equilibrium constant for the pyridine reaction with $AlCl_2(SG)_n$ was so large, complete complexation of the base at low concentrations could be assumed, yielding the enthalpy shown above. A calorimetric titration of this solid acid with 2,6-lutidine showed that the active site was a Brönsted type site. This result was confirmed with an infrared titration of the solid. Uv/vis spectrophotometry also confirmed that the catalyst is deactivated by the loss of HCl.

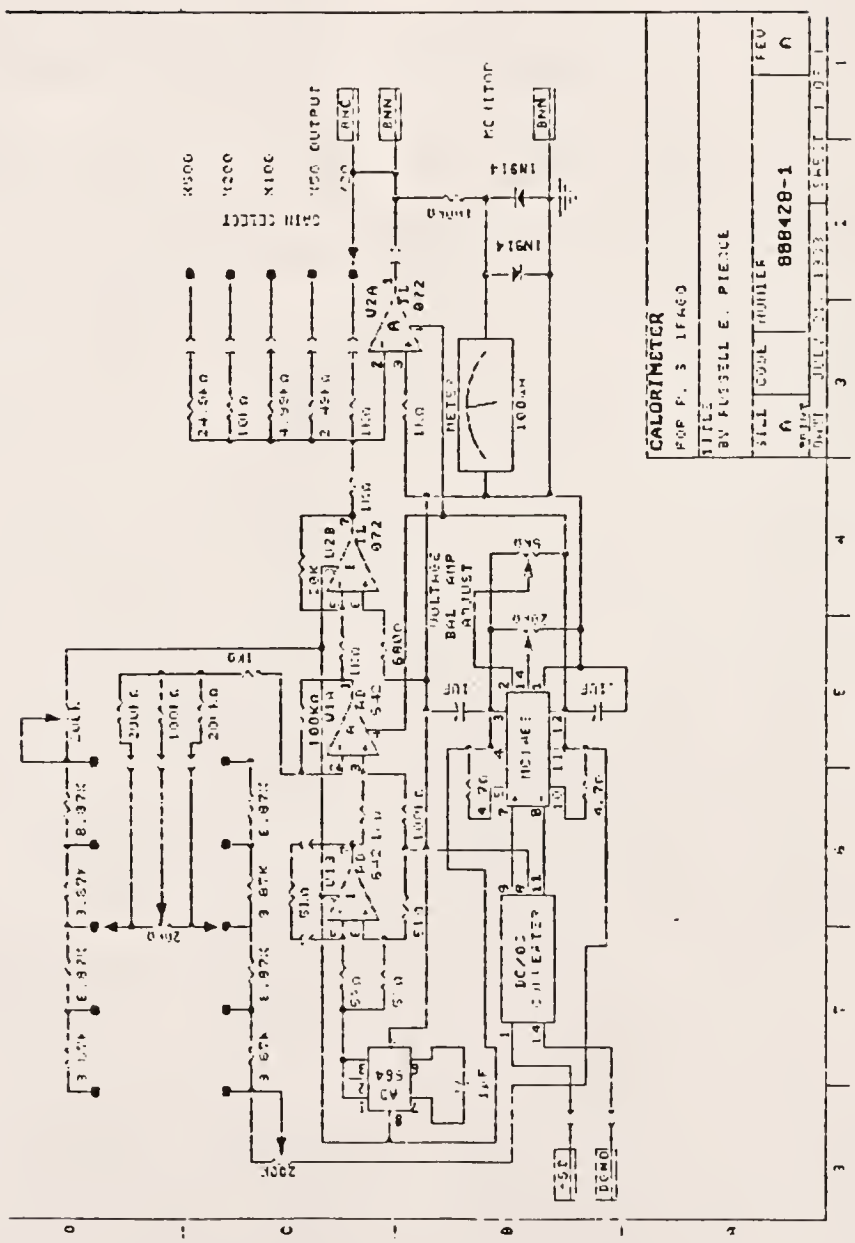
An investigation of phosphotungstic acid revealed another difficulty with solution calorimetry of solids. This solid acid has a very low surface area, making it difficult to obtain measurable heats in the calorimetric titration. The "pseudo liquid phase" property of phosphotungstic acid allowed a switch to a polar solvent in order to obtain heats. Upon dehydration of this acid, its acidity continued to increase. Evacuation at elevated temperatures gave rise to different strength sites on the same solid, whereas the untreated and calcined acid had only one type of site. These sites were also found to be Brönsted sites by calorimetry with 2,6-lutidine and infrared spectroscopy.

The difficulty in determining small base concentrations in solution was encountered again in the investigation of HY zeolite. From the calorimetry data it seems apparent that there are three different discernable sites for pyridine adsorption on the sample calcined at 350 °C. It was confirmed by FTIR that the sites present on HY calcined at 350 °C are Brönsted sites and that a majority of these are converted to Lewis sites on the zeolite calcined at 650 °C. Titration of HY calcined at 350 °C with a series

of bases led to a determination of $E_A = 7.15$ and $C_A = 2.74$. These values indicate that this is an extremely strong acid with predominately electrostatic character. Further work in the Drago group in the large field of zeolites includes titration of HY zeolite with more bases to better determine the above E and C values. Other work includes the investigation of other acidic zeolites (e.g. H-ZSM-5).

In conclusion, the cal-ad method is a powerful tool for the determination of surface thermodynamics. Some systems are difficult to study, but there are still ways to obtain meaningful data. Other future work for the systems that led to the difficulty in obtaining probe concentrations remaining in solution could include an investigation of the solid acids with a weaker base than pyridine. This may lead to a smaller equilibrium constant, thus allowing its concentration to be determined. Benzonitrile may be a good probe to try since it is a weaker base than pyridine and it also absorbs in the UV. Finding good probe molecules which are UV/vis active is another of the difficulties encountered in this type of work.

# APPENDIX I
# SCHEMATIC OF ELECTRONICS



APPENDIX II
PASCAL PROGRAM FOR DATA ACQUISITION

```
{$R+}    {Range checking on}
{$B+}    {Boolean complete evaluation on}
{$S+}    {Stack checking on}
{$I+}    {I/O checking on}
{$N+}    {Numeric coprocessor}
{$E+}    {Numeric coprocessor emulation}
{$M 65500,16384,655360} {Turbo 3 default stack and heap}

 Program IBM_Data_Aquisition_and_Control_Board_for_Calorimeter;
  {This Program was written by Larry Chamusco ongoing updates}
  { It is for the collection of analog data and calculation }
  { of Heats of reaction from the calorimeter.              }

Uses
  Crt,
  Dos,
  GDriver,
  Printer,
  GKernel,
  GWindow,
  GShell,
  Engine;


Type            {Using double for both emulation and 87-proc}
  Float = Double;

type
  BridgeTypes     = (A, B);
  FileTypes       = (New, Old);
  WCursorTypes    = (Start, Stop);
  ZcursorTypes    = (StartPre, StopPre, Inf, StartPst, StopPst);
  Axis            = (XP, YP1, YP2);
  CursorMovement = (Small, Med, Large);
```

```
  CalHeaderT     = RECORD
                   Title          : String[80];
                   Acid,      ConcA,
                   Base,      ConcB,
                   Syringe,   Size,
                   Cell,      Volume,
                   Solvent,
                   Date           : String[10];
                   Bridge         : Char;
                   MaxV,
                   MinV           : Float;
                   END;


var
  CalHeader    : CalHeaderT;
  FileType     : FileTypes;
  NumbSec      : String[9];
  TypeDef      : String[3];
  Temp         : String[10];
  FileName,
  Blank        : String[8];
  BackSlash,
  SourceFile,
  Path,
  PathNow,
  PathInitial : String[40];
  Bridge       : BridgeTypes;
  BridgeIs     : Array[A..B] OF Char;
  FileIs       : Array[New..Old] OF String[3];
  CursorMvSz   : CursorMovement;
  OutputFile,
  HeaderFile   : Text;
  CurrentWindow : ARRAY[1..2] OF String[5];
  Source       : FILE OF Float;
  SizeOf       : ARRAY [Small..Large] OF String[3];
  SizeOfM      : ARRAY [Small..Large] OF Integer;
  Key,
  Ans          : Char;
  Channel,
  CardNumber,
  VoltageOffset,
  VoltageRange,
  TimeIs,
```

```
NextTime,
Wait,
StopKrunch,
XPoint,
Samples,
HighestX,
Direction,
PathL,
WindowIs,
SizeIs,
EndZoom,
EndTrace,
I,
J,
K,
StepIs,
NextOne     : Integer;
M1,M2,
B1,B2,
X,
Y1,Y2,
Deflection,
TempData,
NewData,
AvgData,
MaxV,
MinV,
VMax,
VMin        : Float;
Hour,
Min1,
Min2,
Sec,
CentiSec,
Year,
Month,
Day,
DayofWeek   : Word;
CalTrace    : PlotArray;
OldLine     : Array [1..2,1..4] OF Float;
ZCursorIs   : ARRAY [StartPre..StopPst] OF String[8];
ZCursor     : ARRAY [StartPre..StopPst,XP..YP2] OF Float;
WCursorIs   : ARRAY [Start..Stop] OF String[5];
WCursor     : ARRAY [Start..Stop,XP..YP2] OF Float;
```

```
  CrntZCursor : ZCursorTypes;
  CrntWCursor : WCursorTypes;
  OutputFileOpen,
  HeaderFileOpen,
  SourceOpen,
  FirstCall,
  TimeTo,
  OldLines,
  InGraphics,
  More,
  Quit,
  Collect,
  OverWrite,
  Ok,
  FileExists,
  Next        : Boolean;


const
  F1 = #59;    F6 = #64;
  F2 = #60;    F7 = #65;
  F3 = #61;    F8 = #66;
  F4 = #62;    F9 = #67;
  F5 = #63;    F10 =#68;
       Alt_S = #31;
       Alt_X = #45;
       Alt_Z = #44;
       Alt_Q = #16;
       Alt_C = #46;
       Alt_P = #25;
       Left  = #75;
       Right = #77;


Procedure SetUp;                {Set the Initial Settings}
  begin
    FileIs[OLD] := 'OLD';
    FileIs[NEW] := 'NEW';
    BridgeIs[A] := 'A';
    BridgeIs[B] := 'B';
    Blank       := '        ';
    PathInitial := 'C:\ZData\';
    ZCursorIs[StartPre] := 'StartPre';
    ZCursorIs[StopPre]  := 'StopPre';
```

```
    ZCursorIs[Inf]      := 'Inflect';
    ZCursorIs[StartPst] := 'StartPst';
    ZCursorIs[StopPst]  := 'StopPst';
    WCursorIs[Start]    := 'Start';
    WCursorIs[Stop]     := 'Stop';
    SizeOf[Small]       := '  1';
    SizeOf[Med]         := ' 10';
    SizeOf[Large]       := '100';
    CursorMvSz          := Small;
    SizeOfM[Small]      := 1;
    SizeOfM[Med]        := 10;
    SizeOfM[Large]      := 100;
    CurrentWindow[1]    := 'Whole';
    CurrentWindow[2]    := 'Zoom';
    WindowIs            := 1;
    HighestX            := MaxPlotGlb;
    Quit                := FALSE;
    FirstCall           := TRUE;
    CardNumber    := 0;
    VoltageRange  := 10;
    VoltageOffset := 5;
    OutputFileOpen  := FALSE;
    HeaderFileOpen  := FALSE;
    SourceOpen      := FALSE;
    Wait        := 200;
  end;   {SetUp}

Procedure SetInitialConditions;
  begin
    FileType := New;          {New/Old}
    FileName := Blank;        {Blank := '        ';}
    PathNow  := PathInitial;  {PathInitial := 'C:\ZData\';}
    Bridge   := A;            {A/B = Channels 0/1}
    InGraphics := FALSE;
    MaxV     :=  5;
    MinV     := -5;
    OldLines := FALSE;
    OverWrite := FALSE;
    Quit := FALSE;
  end;   {SetInitialConditions}


Procedure WriteMainMenu;
  begin
```

```
    ClrSCR;
    NormVideo;
    GotoXY(9,2);
    Write('Calorimeter Computer Control Software');
    GotoXY(9,3);
    Write('By LARRY CHAMUSCO');
    GotoXY(5,5);
    Write('F1 - (OLD/NEW)');
    GotoXY(31,5);
    Write('File Name :_____.Dat');
    GotoXY(5,6);
    Write('F2 - To Change Path..... Path =');
    GotoXY(5,7);
    Write('F3 : Bridge');
  end;   {WriteMainMenu}


Procedure FillMainMenu;
  begin
    GoToXY(19,5);
    Write(FileIs[FileType]);
    GoToXY(41,5);
    Write(FileName);
    GoToXY(41,6);
    Write(PathNow);
    GoToXY(19,7);
    Write(BridgeIs[Bridge]);
    GoToXY(32,9);
    Write('Alt-S to CONTINUE');
  end;   {FillMainMenu}


Procedure Changes;
  Procedure ChangeFileType;
    begin
      GoToXY(19,5);
      If FileType = OLD then
         FileType := NEW
         ELSE
         FileType := OLD;
      Write(FileIs[FileType]);
    end;    {ChangeFileType}
  Procedure ChangePath;
    begin
```

```
    GoToXY(41,6);
    ReadLn(PathNow);
    PathL := Length(PathNow);                    {Check Path Validity}
    BackSlash := Copy(PathNow,PathL,1);
    If (BackSlash <> '\') then
      PathNow := PathNow + '\';
      Path := Copy(Pathnow,1,PathL);
    {$I-}
      ChDir(Path);
      If (IOResult = 0) then
         Ok := TRUE
      Else
        Begin
          Ok := FALSE;
          PathNow := PathInitial;
        end;  {END ELSE}
    {$I+}
    GoToXY(41,6);
    Write(PathNow);
  end;    {ChangePath}
Procedure ChangeBridge;
  begin
    GoTOXY(19,7);
    If Bridge = B then
      Bridge := A
      ELSE
      Bridge := B;
    Write(BridgeIs[Bridge]);
  end;    {ChangeBridge}

begin
  Next := FALSE;
  GoToXY(42,5);
  Write(Blank);
  GoToXY(42,5);
  Repeat
   GoToXY(42,5);
   Key := ReadKey;
   If Key = #0 then
      begin
        Key := ReadKey;
        Case Key of
            F1  : ChangeFileType;
            F2  : ChangePath;
```

```
            F3  : ChangeBridge;
          Alt_Q  : Exit;
          Alt_S  : If (FileName < > Blank) then Next := TRUE;
          Alt_X  :  Begin
                    If InGraphics then
                      begin
                        ResetWindowStack;
                        LeaveGraphic;
                      end;
                    EXIT;
                  end;

        end; {END Key Case}
      end  {END IF Key}
      Else If (Key IN ['A'..'Z']) or (Key IN ['a'..'z']) then
        begin
          Write(Key);
          ReadLn(FileName);
          FileName := Key + FileName;
        end;
  Until Next;
end;   {Changes}


Procedure WriteHeader;
  begin
  ClrSCR;
  GoToXY(5,2);
  Write('DATE :');
  GoToXY(5,3);
            W     r     i     t     e     (     '     T     i     t     l     e
:[_____________________________________________________________]');
  GoToXY(5,5);
  Write('Solvent :[_____________]');
  GoToXY(5,6);
  Write('ACID    :[_____________]');
  GoToXY(30,6);
  Write('ACID CONC. :[_____________]');
  GoToXY(5,7);
  Write('BASE    :[_____________]');
  GoToXY(30,7);
  Write('BASE CONC. :[_____________]');
  GoToXY(5,8);
  Write('SYRINGE :[_____________]');
```

```
  GoToXY(30,8);
  Write('SIZE       :[__________]');
  GoToXY(5,9);
  Write('CELL    :[__________]');
  GoToXY(30,9);
  Write('VOLUME     :[__________]');
  GoToXY(5,10);
  Write('BRIDGE  :[__________]');
  GoToXY(5,11);
  Write('MaxV    :');
  GoToXY(5,12);
  Write('MinV    :');
  end;    {WriteHeader}


Procedure FillHeader;
  begin
    Assign(HeaderFile,PathNow + FileName +'.hdr');
    Ok := FALSE;
    {$I-}
      Reset(HeaderFile);
      If IOResult < > 0 then
          If (FileType = OLD) then
             begin
               GoToXY(30,1);
               Write('No Header File!');
               Ok := TRUE;
             end         {END IF OLD}
      else
        HeaderFileOpen := TRUE;
    {$I+}
    If (FileType = NEW) OR (Ok) then
      begin
        ReWrite(HeaderFile);
        HeaderFileOpen := TRUE;
        GetDate(Year,Month,Day,DayOfWeek);
        Str(Day,Temp);
        CalHeader.Date := Temp;
        Str(Month,Temp);
        CalHeader.Date := CalHeader.Date + '/' + Temp;
        Str(Year,Temp);
        CalHeader.Date := CalHeader.Date + '/' + Temp;
        GoToXY(12,2);
        Write(CalHeader.Date);
```

```
WITH CalHeader DO
  begin
    GotoXY(13,3);
    ReadLn(Title);
    GoToXY(15,5);
    ReadLn(Solvent);
    GoToXY(15,6);
    ReadLn(Acid);
    GoToXY(43,6);
    ReadLn(ConcA);
    GoToXY(15,7);
    ReadLn(Base);
    GoToXY(43,7);
    ReadLn(ConcB);
    GoToXY(15,8);
    ReadLn(Syringe);
    GoToXY(43,8);
    ReadLn(Size);
    GoToXY(15,9);
    ReadLn(Cell);
    GoToXY(43,9);
    ReadLn(Volume);
    WriteLn(HeaderFile,Title);
    WriteLn(HeaderFile,Date);
    WriteLn(HeaderFile,Solvent);
    WriteLn(HeaderFile,Acid);
    WriteLn(HeaderFile,ConcA);
    WriteLn(HeaderFile,Base);
    WriteLn(HeaderFile,ConcB);
    WriteLn(HeaderFile,Syringe);
    WriteLn(HeaderFile,Size);
    WriteLn(HeaderFile,Cell);
    WriteLn(HeaderFile,Volume);
  end;              {END WITH}
GoToXY(15,10);
WriteLn(BridgeIs[Bridge]);
CalHeader.Bridge := BridgeIs[Bridge];
WriteLn(HeaderFile,CalHeader.Bridge);
GoToXY(15,11);
WriteLn('Unknown');
GoToXY(15,12);
WriteLn('Unknown');
    MinV := -5.0;                    (*Temp Adj*)
    MaxV := 5.0;
```

```
  end
Else
  begin
    WITH CalHeader DO
      begin
        ReadLn(HeaderFile,Title);
        ReadLn(HeaderFile,Date);
        ReadLn(HeaderFile,Solvent);
        ReadLn(HeaderFile,Acid);
        ReadLn(HeaderFile,ConcA);
        ReadLn(HeaderFile,Base);
        ReadLn(HeaderFile,ConcB);
        ReadLn(HeaderFile,Syringe);
        ReadLn(HeaderFile,Size);
        ReadLn(HeaderFile,Cell);
        ReadLn(HeaderFile,Volume);
        ReadLn(HeaderFile,Bridge);
        ReadLn(HeaderFile,MinV);
        ReadLn(HeaderFile,MaxV);
        GoToXY(13,2);
        WriteLn(Date);
        GotoXY(13,3);
        WriteLn(Title);
        GoToXY(15,5);
        WriteLn(Solvent);
        GoToXY(15,6);
        WriteLn(Acid);
        GoToXY(43,6);
        WriteLn(ConcA);
        GoToXY(15,7);
        WriteLn(Base);
        GoToXY(43,7);
        WriteLn(ConcB);
        GoToXY(15,8);
        WriteLn(Syringe);
        GoToXY(43,8);
        WriteLn(Size);
        GoToXY(15,9);
        WriteLn(Cell);
        GoToXY(43,9);
        WriteLn(Volume);
        GoToXY(15,10);
        WriteLn(Bridge);
        GoToXY(15,11);
```

```
          WriteLn(MaxV:7:4);
          GoToXY(15,12);
          WriteLn(MinV:7:4);
        end;          {END WITH}
        MaxV := CalHeader.MaxV;
        MinV := CalHeader.MinV;
        If MaxV = MinV then
         begin
          MaxV := 5.0;
          MinV := -5.0;
         end       {END IF MaxV}
     end;       {END ELSE}
  end;    {FillHeader}


Procedure OpenFiles;
  begin
    Assign(Source,PathNow + FileName +'.dat');
    {$I-}
    Reset(Source);
    {$I+}
    If IOResult = 0
      then
        begin
          FileExists := TRUE;
          SourceOpen := TRUE;
        end
      else FileExists := FALSE;
    If ((FileType = New) and FileExists) then
      begin
        Ok := FALSE;
        Repeat
         GoToXY(5,9);
         ClrEOL;
         Write('File Exists, WARNING, Do You Wish to OVER WRITE? (Y,N)_');
         Ans := ReadKey;
         Case Ans of
             'y','Y' : begin
                         OverWrite := TRUE;
                         Ok := TRUE;
                       end;
             'n','N' : begin
                         OverWrite := False;
                         Changes;
```

```
                    Ok := TRUE;
                  end;
            end; {Ans Case}
        Until Ok;
      end
    else If (FileType = Old) and NOT FileExists then
      begin
        GoToXY(5,9);
        ClrEOL;
        Write('File not found, WARNING, You must make changes!');
        Changes;
      end;                    {End else If}
    If (FileType = NEW) AND NOT (FileExists) OR OverWrite then
      begin
        Rewrite(Source);
        SourceOpen := TRUE;
      end
  end;    {OpenFiles}


Procedure DisplayInfo;
  begin
    WriteHeader;
    Fillheader;
    Collect := FALSE;
    GoToXY(10,14);
    Write('Alt-S to continue');
    Repeat
      Ans := Readkey;
      If Ans = Alt_S then Collect := TRUE;
    Until Collect;
  end;   {DisplayInfo}


Procedure DrawInZCursors(ZoomTrace:PlotArray);
 var
    K,
    I      : Integer;
    WhichZ : ZCursorTypes;
  begin
    WhichZ := StartPre;
    I := 1;
    SelectWorld(2);
    SelectWindow(2);
```

```
    For WhichZ := StartPre TO StopPst DO
      begin
        ZCursor[WhichZ,XP] := (I/6) * EndZoom;      {Initial X Position Ith Cursor}
        If WhichZ < Inf then
          begin
           ZCursor[WhichZ,YP1] := VMin;          {Top Of Window}
           ZCursor[WhichZ,YP2] := ZoomTrace[Trunc(ZCursor[WhichZ,XP]),2];{Top
of Trace}
          end          {END IF}
        Else If WhichZ > Inf then
          begin
           ZCursor[WhichZ,YP1] := ZoomTrace[Trunc(ZCursor[WhichZ,XP]),2];{Top
Of Trace}
           ZCursor[WhichZ,YP2] := VMax;          {Bottom of Window}
          end          {END ELSE IF}
        Else
          begin
            ZCursor[WhichZ,YP1] := VMin;          {Top Of Window}
            ZCursor[WhichZ,YP2] := VMax;          {Bottom of Window}
          end;          {END ELSE}
        I := I + 1;
        DrawLine(ZCursor[WhichZ,XP],ZCursor[WhichZ,YP1],ZCursor[WhichZ,XP],
                 ZCursor[WhichZ,YP2]);
      end;          {END FOR WHICHZ}
  end;    {DrawInZCursors}



Procedure Zoom(var ZoomTrace:PlotArray);
var
  I,
  I1 : Integer;
 begin
   If (FileType = NEW) AND (StopKrunch < > 0) then
     begin
      StepIs := 8;
      If (WCursor[Start,XP] < = StopKrunch) then
        begin                              {For Collection Routine}
          I := Trunc(StepIs * WCursor[Start,XP]);
        end              {END IF WCursor}
      else
        I := Trunc((StepIs * StopKrunch) + (WCursor[Start,XP] - StopKrunch));
      If (WCursor[Stop,XP] < = StopKrunch) then
        begin
```

```
      J := Trunc(StepIs * WCursor[Stop,XP]);
    end
  else
    J := Trunc((StepIs * StopKrunch) + (WCursor[Stop,XP] - StopKrunch));
 end                    {END IF FILETYPE AND STOPKRUNCH}
else
 begin
   I := Trunc(StepIs * WCursor[Start,XP]);
   J := Trunc(StepIs * WCursor[Stop,XP]);
 end;

I1 := 0;
VMin := MaxV;
VMax := MinV;
If NOT (SourceOpen) then
 begin
   Reset(Source);
   SourceOpen := TRUE;
 end;           {END IF NOT SOURCEOPEN}
For K := I TO J DO
 begin
 I1 := I1 + 1;
 Seek(Source,K);
 Read(Source,ZoomTrace[I1,2]);
 ZoomTrace[I1,1] := I1;
 If VMax < ZoomTrace[I1,2] then
   begin
     VMax := ZoomTrace[I1,2];
   end;             {END IF VMAX}
 If VMin > ZoomTrace[I1,2] then
   begin
     VMin := ZoomTrace[I1,2];
   end;             {END IF VMIN}
 end;       {END FOR K}
Close(Source);
SourceOpen := FALSE;
If (VMin < 0) then
 VMin := VMin + (VMin/10)
else
  VMin := VMin - (VMin/10);
VMax := VMax + (VMax/10);
DefineWorld(2,0,VMin,I1,VMax);
SelectWorld(2);
SelectWindow(2);
```

```
    SetBackground(0);
    DrawPolygon(ZoomTrace,1,-I1,0,1,0);
    DrawBorder;
    EndZoom := I1;
    K := I1;
    DrawInZCursors(ZoomTrace);
  end;    {Zoom}


Procedure MoveWCursor;
  begin
    SelectWorld(1);
    SelectWindow(1);
    SetColorBlack;
    DrawLine(WCursor[CrntWCursor,XP],WCursor[CrntWCursor,YP1],
            WCursor[CrntWCursor,XP],WCursor[CrntWCursor,YP2]);
    SetColorWhite;
    DrawPoint(CalTrace[Trunc(WCursor[CrntWCursor,XP]),1],
             CalTrace[Trunc(WCursor[CrntWCursor,XP]),2]);
    WCursor[CrntWCursor,XP] := SizeOfM[CursorMvSz] * Direction
                              + WCursor[CrntWCursor,XP];
    If WCursor[CrntWCursor,XP] < 1 then
      WCursor[CrntWCursor,XP] := 1;
    If WCursor[CrntWCursor,XP] > EndTrace then
      WCursor[CrntWCursor,XP] := EndTrace;
    DrawLine(WCursor[CrntWCursor,XP],WCursor[CrntWCursor,YP1],
            WCursor[CrntWCursor,XP],WCursor[CrntWCursor,YP2]);
  end;    {MoveWCursor}


Procedure EraseOldLines;
var
   I : Integer;
  begin
    SelectWorld(2);
    SelectWindow(2);
    SetColorBlack;
    For I := 1 TO 2 DO
      begin
        DrawLine(OldLine[I,1],OldLine[I,2],OldLine[I,3],OldLine[I,4]);
      end;    {END FOR I}
    SetColorWhite;
  end;    {EraseOldLines}
```

```
Procedure Calculate;
var
 NumWhat : String[8];
 begin
   GoToXY(36,3);
   If (TypeDef = 'Cal') then
     begin
       Write('# of SECONDS');
       GoToXY(49,3);
       ReadLn(NumbSec);
       GoToXY(49,3);
       ClrEOL;
       Write(NumbSec,' ; Deflection : ',Deflection:8:4);
       NumWhat := ',# Sec.,';
     end
     else                                {EXP. Injection}
     begin
       Write('# Injection ');
       GoToXY(49,3);
       ReadLn(NumbSec);
       GoToXY(49,3);
       ClrEOL;
       Write(NumbSec,' ; Inj. Deflt : ',Deflection:8:4);
       NumWhat := ',# Inj.,';
     end;
   Append(OutputFile);
   WriteLn(OutputFile,Deflection:7:4,',',TypeDef,NumWhat,NumbSec:9);
   Close(OutputFile);
   OutputFileOpen := FALSE;
 end;    {Calculate}


Procedure FindMB;
 begin
   X := ZCursor[Inf,XP];
   M1 := (ZCursor[StopPre,YP2]-ZCursor[StartPre,YP2])
         /(ZCursor[StopPre,XP]-ZCursor[StartPre,XP]);
   M2 := (ZCursor[StopPst,YP1]-ZCursor[StartPst,YP1])
         /(ZCursor[StopPst,XP]-ZCursor[StartPst,XP]);
   B1 := ZCursor[StartPre,YP2]-(M1 * ZCursor[StartPre,XP]);
   B2 := ZCursor[StartPst,YP1]-(M2 * ZCursor[StartPst,XP]);
   Y1 := B1 + (M1 * X);
   Y2 := B2 + (M2 * X);
 end;    {FindMB}
```

```
Procedure FillOldLines;
  begin
    OldLine[1,1] := ZCursor[StartPre,XP];
    OldLine[1,2] := ZCursor[StartPre,YP2];
    OldLine[1,3] := X;
    OldLine[1,4] := Y1;
    OldLine[2,1] := X;
    OldLine[2,2] := Y2;
    OldLine[2,3] := ZCursor[StopPst,XP];
    OldLine[2,4] := ZCursor[StopPst,YP1];
    OldLines := TRUE;
  end;    {FillOldLines}


Procedure DrawIntLines;
  begin
    If (OldLines = TRUE) then
      begin
        EraseOldLines;
      end;    {END IF OldLines}
    SelectWorld(2);
    SelectWindow(2);
    FindMB;
    FillOldLines;
    DrawLine(ZCursor[StartPre,XP],ZCursor[StartPre,YP2],X,Y1);
    DrawLine(X,Y2,ZCursor[StopPst,XP],ZCursor[StopPst,YP1]);
    Deflection := Y2 - Y1;
    GoToXY(55,3);
    Write('Deflection : ',Deflection:7:4);
  end;    {DrawIntLines}


Procedure MoveZCursor(ZoomTrace:PlotArray);
  begin
    SelectWorld(2);
    SelectWindow(2);
    SetColorBlack;
    DrawLine(ZCursor[CrntZCursor,XP],ZCursor[CrntZCursor,YP1],
             ZCursor[CrntZCursor,XP],ZCursor[CrntZCursor,YP2]);
    SetColorWhite;
    DrawPoint(ZoomTrace[Trunc(ZCursor[CrntZCursor,XP]),1],
              ZoomTrace[Trunc(ZCursor[CrntZCursor,XP]),2]);
    ZCursor[CrntZCursor,XP] := (SizeOfM[CursorMvSz] * Direction)
```

```
                        + ZCursor[CrntZCursor,XP];
    If ZCursor[CrntZCursor,XP] < 1 then
      ZCursor[CrntZCursor,XP] := 1;
    If ZCursor[CrntZCursor,XP] > K then
      ZCursor[CrntZCursor,XP] := K;
       If CrntZCursor < Inf then
         begin
                        ZCursor[CrntZCursor,YP2]    :=
ZoomTrace[Trunc(ZCursor[CrntZCursor,XP]),2];{Top of Trace}
         end          {END IF}
       Else If CrntZCursor > Inf then
         begin
                        ZCursor[CrntZCursor,YP1]    :=
ZoomTrace[Trunc(ZCursor[CrntZCursor,XP]),2];{Top Of Trace}
         end;         {END ELSE IF}
    DrawLine(ZCursor[CrntZCursor,XP],ZCursor[CrntZCursor,YP1],
            ZCursor[CrntZCursor,XP],ZCursor[CrntZCursor,YP2]);
  end;    {MoveZCursor}


Procedure DrawInWCursors;
  begin
    WCursor[Start,XP] := 50;              {Initial X Position 1st Cursor}
    WCursor[Stop ,XP] := 100;             {Initial X Position 2nd Cursor}
    WCursor[Start,YP1] := MinV;           {Top Of Window}
    WCursor[Stop ,YP1] := MinV;           {Top of Window line 2}
    WCursor[Start,YP2] := MaxV;           {Bottom of Window}
    WCursor[Stop ,YP2] := MaxV;           {Bottom of Window line 2}
    DrawLine(WCursor[Start,XP],WCursor[Start,YP1],WCursor[Start,XP],
            WCursor[Start,YP2]);
    DrawLine(WCursor[Stop,XP],WCursor[Stop,YP1],WCursor[Stop,XP],
            WCursor[Stop,YP2]);
  end;    {DrawInWCursors}


Procedure SetupDisplay;
  begin
    ClrSCR;
    If NOT (InGraphics) then
       begin
         InitGraphic;
         InGraphics := TRUE;
       end
    Else
```

```
      EnterGraphic;
    CrntZCursor := StartPre;
    CrntWCursor := Start;
    GoToXY(30,2);
    Write('CALOGRAM  COLLECTION');
    GoToXY(5,3);
    Write('F3 : Deflection Exp/Calb');
    GoToXY(1,14);
    Write('F5 - CURSOR(          )');
    GoToXY(26,14);
    Write('F8 - WINDOW(      )');
    GoToXY(48,14);
    Write('F9 : DRAW DEFLECTION');
    GoToXY(1,15);
    Write('F6 - ZOOM CURSOR(     )');
    GoToXY(26,15);
    Write('F7 - CURSOR MOVEMENT x(   )');
    GoToXY(57,15);
    Write('Alt-C : SAVE DEFLECTION');
    GoToXY(5,16);
    Write('Alt-Z : ZOOM');
    GoToXY(20,16);
    Write('Alt-Q : END COLLECTION');
    GoToXY(45,16);
    Write('F10 - END SESSION');
    If MinV = MaxV then
      begin
        MinV := -5;
        MaxV := 5;
      end;    {END IF MinV}
  end;    {SetupDisplay}


Procedure FillInDisplay;
  begin
    GoToXy(13,14);
    Write(ZCursorIs[CrntZCursor]);
    GoToXy(18,15);
    Write(WCursorIs[CrntWCursor]);
    GoToXy(49,15);
    Write(SizeOf[CursorMvSz]);
    GoToXy(38,14);
    Write(CurrentWindow[WindowIs]);
  end;    {FillInDisplay}
```

```
Procedure WindowDef;
  begin
    DefineWorld(1,0,MinV,HighestX,MaxV);
    DefineWindow(1,0,238,XMaxGlb,YMaxGlb);
    DefineWindow(2,0,54,XMaxGlb,180);
    SelectWindow(1);
    DrawBorder;
    SelectWindow(2);
    DrawBorder;
  end;   {WindowDef}


Procedure DrawCalogram;
var
   I1 : Integer;
  begin
    I := 0;
    SizeIs := FileSize(Source);
    If (SizeIs < = HighestX) then
       While NOT EOF(Source) do
            begin
              I := I + 1;
              Read (Source, CalTrace[I,2]);
              CalTrace[I,1] := I;
              StepIs := 1;
            end      {END WHILE}
    else
      begin
        NextOne := 1;
        StepIs := Trunc(SizeIs DIV HighestX) +1;
        Repeat
          I := I + 1;
          Seek(Source,NextOne);
          Read(Source,CalTrace[I,2]);
          CalTrace[I,1] := I;
          NextOne := NextOne + StepIs;
          GoToXY(5,2);
          Write('X: ',CalTrace[I,1]:6:4,' ,Y: ',CalTrace[I,2]:6:4);
        Until ((EOF(Source)) OR (I = HighestX) OR (NextOne > SizeIs));
      end;                    {END IF/ELSE}
    Close(Source);
    SourceOpen := FALSE;
    MinV := MinV - (MinV * 0.1);
```

```
    MaxV := MaxV + (MaxV * 0.1);
    SetupDisplay;
    FillInDisplay;
    WindowDef;
    SelectWorld(1);
    SelectWindow(1);
    EndTrace := I;
    I1 := -I;
    DrawPolygon(CalTrace,1,I1,0,1,0);
  end;    {DrawCalogram}


Procedure WhichKey;
 var
    ZoomTrace : PlotArray;
 begin                    (*Meat of the Workup data*)
     If Key = #0 then
       begin
         Key := ReadKey;
         Case Key of
             F3        : begin                      {Type of Deflection}
                         GoToXY(31,3);
                         Write('   ');
                         GoToXY(31,3);
                         If (TypeDef = 'Cal') then
                           TypeDef := 'EXP'
                         Else
                           TypeDef := 'Cal';
                         Write(TypeDef);
                        end;
             F5        : begin                    {Change Zoomed Cursor}
               {StartPre, StopPre, Inf, StartPst, StopPst}
                          If CrntZCursor = StopPst then
                            begin
                              CrntZCursor := StartPre;
                            end       {END IF CRNTZCURSOR}
                          Else
                            begin
                              Inc(CrntZCursor);
                            end;       {END ELSE}
                         GoToXY(13,14);
                         Write(ZCursorIs[CrntZCursor]:8);
                        end;
             F6        : begin                    {Change To Zoom Cursor}
```

```
                {Start, Stop}
               If CrntWCursor = Stop then
                begin
                  CrntWCursor := Start;
                end       {END IF CRNTWCURSOR}
               Else
                begin
                  Inc(CrntWCursor);
                end;       {END ELSE}
               GoToXY(18,15);
               Write(WCursorIs[CrntWCursor]:5);
              end;
F7          : begin                    {Cursor Moverment Size}
                {Small, Med, Large}
               If CursorMvSz = Large then
                begin
                  CursorMvSz := Small;
                end       {END IF CURSORMVSZ}
               Else
                begin
                  Inc(CursorMvSz);
                end;       {END ELSE}
               GoToXY(49,15);
               Write(SizeOf[CursorMvSz]:3);
              end;
F8          : begin                          {Which Window}
               If WindowIs = 1 then
                 WindowIs := 2
               Else
                 WindowIs := 1;
               GoToXY(38,14);
               Write(CurrentWindow[WindowIs]:5);
              end;
F9          : begin                      {DrawInterceptLines}
               DrawIntLines;
              end;
F10, ALT_X : begin                             {Exit and Quit}
               Quit := TRUE;
              end;
Left        : begin                       {Move Cursor Left}
               Direction := -1;
               If WindowIs = 1 then
                begin
                  MoveWCursor;
```

```
                    end    {END IF WindowIs}
                  Else
                    begin
                    MoveZCursor(ZoomTrace);
                    end;   {END ELSE}
                end;
        Right     : begin                    {Move Cursor Right}
                  Direction := 1;
                  If WindowIs = 1 then
                    begin
                      MoveWCursor;
                    end    {END IF WindowIs}
                  Else
                    begin
                      MoveZCursor(ZoomTrace);
                    end;   {END ELSE}
                end;
        ALT_C     : Calculate;              {Calculate Deflection}
        ALT_P     : begin                   {Print a Screen Dump}
                  HardCopy(FALSE, 1);
                  end;
        ALT_Z     : begin                        {Display Zoom}
                  If FileType = NEW then
                  begin
                    Close(Source);
                    SourceOpen := FALSE;
                  end;          {END IF FILETYPE}
                  Zoom(ZoomTrace);       {Display Zoomed Portion}
                  If SourceOpen = FALSE then
                    begin
                      Reset(Source);
                      SourceOpen := TRUE;
                    end;          {END IF SOURCEOPEN}
                end;
        ALT_Q     : Quit := TRUE;                          {Exit}
      end;     {END CASE KEY}
    end;     {END IF KEY}
end;   {WhichKey}


Procedure CloseAllFiles;
 begin
                { OutputFile, HeaderFile    : Text
                  Source                    : FILE OF Float}
```

```
    If OutputFileOpen then
      begin
        Close(OutputFile);
        OutputFileOpen := FALSE;
      end;
    If HeaderFileOpen then
      begin
        WriteLn(HeaderFile,CalHeader.MinV);
        WriteLn(HeaderFile,CalHeader.MaxV);
        Close(HeaderFile);
        HeaderFileOpen := FALSE;
      end;
    If SourceOpen then
      begin
        Close(Source);
        SourceOpen := FALSE;
      end;
  end;    {CloseAllFiles}


Procedure WorkupData;
  begin
    Quit := FALSE;
    DrawCalogram;
    DrawInWCursors;
    Repeat
      IF KeyPressed then
        begin
          Key := ReadKey;
          If Key = #0 then
            begin
              WhichKey;
            end;     {END IF KEY}
        end;     {END IF KEYPRESSED}
    Until QUIT;
    CloseAllFiles;                              (*Close all files!!*)
  end;   {WorkupData}

                (*This section is for the collection of data*)

Procedure DrawTrace;
var
   KrunchIs,
   I, K       : Integer;
```

```
  begin
    KrunchIs := 8;              {Krunch Factor, to squeeze Data}
    I := StopKrunch;
    K := 1;
    Repeat
      K := K + KrunchIs;
      If (K > HighestX) then
        K := HighestX;
      I := I + 1;
      CalTrace[I,2] := CalTrace[K,2];
    Until (K = HighestX);
    DrawPolygon(CalTrace,1,-I,0,1,0);
    XPoint := I;
    StopKrunch := I;
  end;    {DrawTrace}


Procedure ClearWindow;
  begin
    SelectWorld(1);
    SelectWindow(1);
    SetBackground(0);
    DrawBorder;
  end;    {ClearWindow}


Procedure RedrawPlot;
  begin
    ClearWindow;
    DrawTrace;

  end;    {RedrawPlot}


Procedure ReadData(var TempData:Float);
  begin
    Channel := Ord(Bridge);
    If FirstCall then
      begin
        InitDevice(CardNumber,TRUE);
        FirstCall := FALSE;
      end;      {END IF FIRSTCALL}
    TempData := ReadAnalogData(CardNumber,Channel);
    TempData := ConvertDataToVolts(TempData,VoltageRange,VoltageOffset);
```

```
  end;    {ReadData}


Procedure GetAPoint;
var
   I : Integer;
  begin            (*Get the point, average the point, inc. X*)
    For I := 1 TO Samples DO
      begin
        ReadData(TempData);
        If I = I then
         begin
           AvgData := TempData;
         end         {END IF I}
      else
        begin
         AvgData := AvgData + TempData;
        end;        {END ELSE IF I}
      end;      {END FOR SAMPLES}
    AvgData := AvgData / Samples;                {Signal Average}
    XPoint := XPoint + 1;
    NewData := (AvgData + NewData) / 2;          {Lag Filter}
    CalTrace[XPoint,1] := XPoint;
    CalTrace[XPoint,2] := NewData;
    If (XPoint = 1) then
      begin
        CalHeader.MinV := NewData;
        CalHeader.MaxV := NewData;
      end;     {END IF XPoint}
    If (NewData < MinV) then
      begin
        CalHeader.MinV := NewData;
        MinV := NewData;
      end;         {END IF NEWDATA}
    If (NewData > MaxV) then
      begin
        CalHeader.MaxV := NewData;
        MaxV := NewData;
      end;         {END IF NEWDATA}
    EndTrace := XPoint;
    Seek(Source,FileSize(Source));
    Write(Source,NewData);
  end;    {GetAPoint}
```

```
Procedure DrawAPoint;
  begin
    SelectWorld(1);
    SelectWindow(1);
    DrawPoint(XPoint,NewData);
  end;    {DrawAPoint}


Procedure ReadTime;          {This works in 100th's of Seconds}
  begin
    TimeTo := FALSE;
    GetTime(Hour,Min1,Sec,CentiSec);
    TimeIs := CentiSec + (Sec * 100);
    NextTime := TimeIs + Wait;
  end;    {ReadTime}


Procedure CompareTime;       {Compare for next data read}
  begin
    GetTime(Hour,Min2,Sec,CentiSec);
    TimeIs := CentiSec + (Sec * 100);
    If Min2 < > Min1 then
      TimeIs := TimeIs + 6000;
    If TimeIs > = NextTime then
      TimeTo := TRUE;
  end;    {CompareTime}


Procedure CollectData;
 var
    DrawIn : Boolean;
  begin
    DrawIn  := TRUE;
    Samples := 2;
    TimeTo := TRUE;
    SetupDisplay;
    FillInDisplay;
    WindowDef;
    SelectWorld(1);
    SelectWindow(1);
    XPoint := 0;
    StepIs := 1;
    StopKrunch := 0;
```

```
    Repeat
      If TimeTo then
        begin
          GetAPoint;
          DrawAPoint;
          ReadTime;
        end;    {END IF TIMETO}
      IF KeyPressed then
        begin
          Key := ReadKey;
          If Key = #0 then
            begin
              WhichKey;
            end;     {END IF KEY}
        end;     {END IF KEYPRESSED}

      If (XPoint = HighestX) then RedrawPlot;
      If (XPoint >= 101) AND (DrawIn) then
        begin
          DrawInWCursors;
          DrawIn := FALSE;
        end;
      CompareTime;
    Until QUIT;

    CloseAllFiles;                          (*Close all files!!!*)
  end;    {CollectData}


Procedure AskIfMore;
  begin
    ClrSCR;
    More := FALSE;
    Repeat
      GoToXY(5,5);
      Write('Begin again? (Y/N)_');
      Ans := Readkey;
      If Ans in ['y','Y'] then More := TRUE;
    Until Ans in ['y','Y','n','N'];
  end;   {AskIfMore}


begin              {Main program}
 SetUp;
```

```
  Repeat
   ClrSCR;
   SetInitialConditions;
   WriteMainMenu;
   FillMainMenu;
   Changes;
   OpenFiles;
   DisplayInfo;
   Assign(OutputFile,PathNow + FileName + '.cal');
   {$I-}
     Reset(OutputFile);
     If (IOResult < > 0) then
       Rewrite(OutputFile);
   {$I+}
   OutputFileOpen : = TRUE;
   Case FileType of
        New      :  CollectData;
        Old      :  WorkupData;
   end;        {END FileType Case}
   LeaveGraphic;
   AskIfMore;
  Until NOT More;
end.
```

# APPENDIX III
# MANUAL FOR DATA ACQUISITION PROGRAM

The following is a manual for the use of the data acquisition program given in Appendix II. The description of the sample and cell preparation and of the actual experiment are included in Chapter 1. This appendix is solely for the use of the Cal 2 program for calorimetric data acquisition. This program allows the user to determine the size of the deflections while the program is collecting data. This program consists of three levels of menus. The first menu includes the title of the data file and four fields, three of which are controlled by function keys. The second menu is for the display of the header file which contains the information about the titration conditions. The third menu is the acquisition and processing screen.

The main menu contains four fields. The first field is controlled by F1, and is for changing the type of file. The file is changed from new to old, or the reverse, by pressing F1, this is a toggle switch. The second field is for the filename. The cursor resides in this field. If the file type is old and the file does not exist a warning is displayed. If the file type is new and the file already exists, the option is given to overwrite the old file. The third field is controlled by the F2 key. This field is for changing the path to which or from the file is to be stored or retrieved. If the path does not exist, a warning is displayed. The fourth field is for changing the bridge. This is

another toggle switch which alternates between A and B. When the fields are at their desired settings, press Alt-S to continue to the next screen.

The second screen is the second menu. This menu either displays the header of an old file or allows the input of the titration conditions for a new file. After the reading of or input to the header file, press Alt-S to continue to the next screen.

The third screen is the third menu. This screen is for the collection and processing of data. This screen is composed of two windows, ten displayed function keys, and three undisplayed function keys. The two windows include an upper window for an expanded view of a section of data (zoom window), and a lower window for a panoramic view of all the data (whole window). The displayed function keys are F3, F5, F6, F7, F8, F9, Alt-C, Alt-Z, Alt-Q, and F10. The undisplayed function keys are Alt-P, left arrow, and right arrow.

F3 is a toggle switch for alternating between an experimental (EXP) and a calibration (CAL) type of deflection. An experimental deflection is one that is caused by an injection of probe from the syringe. A calorimetric deflection is one that is caused by the use of the heater coil.

F5 is a toggle switch for rotating through the five choices of the work cursors in the zoom window. The choices for the work cursor are StartPre, StopPre, Inf, StartPst, and StopPst. The Inf cursor is for setting the inflection point. The Pre and Pst cursors are set as reference points to draw baselines before and after the inflection respectively. The baselines are drawn in when F9 is pressed. The value of the deflection is not saved until Alt-C is pressed.

F6 is a toggle switch for alternating between Start and Stop. These cursors in the whole window define the region of the calogram to be zoomed in on. Alt-Z is pressed to view the expanded area in the zoom window. The zoom cursors are displayed automatically after a set quantity of data has been collected.

F7 is a toggle switch for rotating through the choices of the cursor movement step size. The choices are 1, 10, and 100 data points. This controls the size of the incremental movement of all the cursors.

F8 is a toggle switch for alternating between the two windows, zoom and whole. This is the method for controlling which set of cursors the left and right arrow keys control.

F9 draws in the enthalpic deflection in the zoom window as defined by the work cursors. If the result is unsatisfactory, the work cursors positions can be changed. By depressing F9 again, the old deflection will be erased and a new one drawn in.

Alt-C saves the value of the enthalpic deflection to a data file on disk in the set path. If it is an EXP heat it is saved with a string declaring it as such. The number of the injection must be entered after Alt-C is depressed. If it is a CAL heat it is saved with a string declaring it as such. The number of seconds the heater coil was on must be entered after Alt-C is depressed.

Alt-Z writes to the zoom window the portion of the data file defined by the zoom cursors in the whole window. The zoom window may be redrawn by resetting the zoom cursors and pressing Alt-Z again.

Both F10 and Alt-Q end the acquisition of data. After the termination of the acquisition a prompt appears asking if the user wishes to remain in the program. If the user responds with either Y or y the program returns to the first menu. If the user responds with either N or n the program is terminated.

Alt-P is a screen dump utility. Pressing Alt-P sends what is currently on the screen to an Epson, or Epson compatible, printer.

The left and right arrow keys control the current cursor of the current window. The left arrow moves the cursor to the left with a step of the size which has been set. The right arrow moves the cursor to the right with a step of the size which has been set. By changing the step size and direction, any data point can be accessed by the cursors.

APPENDIX IV
FORTRAN PROGRAM FOR DATA ANALYSIS

```
      CHARACTER*60 INFILE, OUTFILE
      DIMENSION B(10,100),H(100),P(18),D(18),DIF(100),IFIX(100)
      DIMENSION HH(100),SD(18), BB(6)
      AVGC=0.00
      AVGE=0.00
      WRITE (6,1)
    1 FORMAT (5X,'Name of Data File? ')
      READ (5,'(A)') INFILE
      OPEN (8,FILE=INFILE,STATUS='OLD')
      READ (8,*) NC,GC
      DO 6 I=1,NC
      READ (8,*) B(1,I),H(I)
    6 CONTINUE
      READ (8,*) NE,GE
      N=NC+NE
      DO 7 I=NC+1,N
      READ (8,*) B(1,I),H(I)
    7 CONTINUE
```

```
      READ (8,*) NS, EP, KX
      READ (8,*) (P(I),IFIX(I),I=1,3*NS)
      CLOSE(8)
      DO 5 I=NC+1,N
      AVGE=AVGE+H(I)/NE
    5 CONTINUE
      DO 10 I=1,NC
      AVGC=AVGC+H(I)/NC
      HH(I)=H(I)/GC
   10 CONTINUE
      IF (AVGE.EQ.0) AVGE=1.00
      B(10,100)=AVGC/AVGE
      IF (AVGE.EQ.0.OR.AVGC.EQ.0) B(10,100)=1.00
      DO 15 I=NC+1,N
      HH(I)=H(I)*B(10,100)/GE
   15 CONTINUE
      DO 20 I=1,3*NS
      SD(I)=0.000
      D(I)=P(I)*0.1
      IF (IFIX(I).EQ.1) D(I)=0.000
   20 CONTINUE
      WRITE (6,224)
```

```
224 FORMAT(//5X,'WORKING')
    CALL SIMPLEX(EP,3*NS,NC,N,KX,P,D,HH,B,NS)
    DEVN=0.00
    DO 30 I=1,N
    G=GC
    IF (I.GT.NC) G=GE
    DIF(I)=H(I)-G*CAL(I,P,B,NC,NS)
 30 CONTINUE
    DO 40 I=1,N
    DEVN=DIF(I)**2
    DO 40 IS=1,NS
    L1=3*IS-2
    L2=3*IS-1
    L3=3*IS
    B1=P(L2)*B(1,I)
    IF (I.GT.NC) GO TO 50
    SD(L1)=SD(L1)+(((1.0+B1)/(P(L3)*B1))**2)*DEVN
    SD(L2)=SD(L2)+((((1.0+B1)**2)/(P(L1)*P(L3)*B(1,I)))**2)*DEVN
    SD(L3)=SD(L3)+(((1.0+B1)/(P(L1)*B1))**2)*DEVN
    GO TO 40
 50 SD(L1)=SD(L1)+(((1.0+B1)/B1)**2)*DEVN
    SD(L2)=SD(L2)+((((1.0+B1)**2)/(P(L1)*B(1,I)))**2)*DEVN
```

```
 40 CONTINUE
    DO 60 IS=1,NS
    SD(3*IS-2) = SQRT(SD(3*IS-2)/N)
    SD(3*IS-1) = SQRT(SD(3*IS-1)/N)
    IF (NC.GT.0) SD(3*IS) = SQRT(SD(3*IS)/NC)
 60 CONTINUE
    DO 65 I=1,3*NS
    IF (IFIX(I).EQ.1) SD(I)=-1.00
 65 CONTINUE
    WRITE (6,201)
201 FORMAT (/5X,'Fitting Routinue Completed',
   *//5X,'Name of Output File? ')
    READ (5,'(A)') OUTFILE
    OPEN (7,FILE=OUTFILE)
    IF (NC.GT.0) WRITE (7,200)
200 FORMAT (//3X,'#',6X,'BSOL',11X,'HEXP',11X,'HCAL',11X,
   *'ERR',11X,'PER',/)
    DO 70 I=1,NC
    HCAL1=GC*CAL(I,P,B,NC,NS)
    PER1=ABS(100.0*DIF(I)/H(I))
    WRITE (7,210) I,B(1,I),H(I),HCAL1,DIF(I),PER1
210 FORMAT (2X,I3,3X,E12.6,3(3X,E12.6),3X,F5.2)
```

```
 70 CONTINUE
    IF (NE.GT.0) WRITE (7,202)
202 FORMAT (//3X,'#',6X,'BSOL',11X,'BPDO',11X,'BCAL',11X,'ERR',11X,
   *'PER',/)
    DO 71 I=NC+1,N
    HCAL2=GE*CAL(I,P,B,NC,NS)
    PER2=ABS(100.0*DIF(I)/H(I))
    WRITE (7,211) I-NC,B(1,I),H(I),HCAL2,DIF(I),PER2
211 FORMAT (2X,I3,3X,E12.6,3(3X,E12.6),3X,F5.2)
 71 CONTINUE
    DO 72 IS=1,NS
    WRITE (7,220) (IS,P(I+(IS-1)*3),SD(I+(IS-1)*3),I=1,3)
220 FORMAT (//3X,'n',I1,' is ',E11.5,' with a stand. dev. of ',
   *E11.5,' in mole/g',/3X,'K',I1,' is ',E11.5,
   *' with a stand. dev. of ',E11.5,/3X,'H',I1,' is ',E11.5,
   *' with a stand. dev. of ',E11.5,' in cal/mole')
 72 CONTINUE
    IF (NC.GT.0) WRITE (7,222) GC
    IF (NE.GT.0) WRITE (7,223) GE
222 FORMAT(//3X,'Grams of Solid for calorimetry data is ',E11.5)
223 FORMAT(/3X,'Grams of Solid for equilibrium data is ',E11.5)
    CLOSE (7)
```

```
      STOP
      END
CCCC
```

```
      END
CCCC
```

```
C  the equation.
C
C  The program the number of parameters, NP, the
C  convergence factor, EP, the variables, B, the number
C  of points, N, the maximum number of loops, KX, the
C  measured value, H, initial guesses for parameter, T,
C  and the interval for varying the parameters, D.
C  Set D equal to zero to fix parameter.
C
C  This is a sample of what the function FUNK looks like
C
C      FUNCTION FUNK(H,P,B,N)
C      DIMENSION H(100),P(10),B(10,100)
C      FUNK=0.0
C      DO 10 I=1,N
C      FUNCTION=function you wish to solve parameters for
C      FUNK=FUNK+(H(I)-FUNCTION)**2
C   10 CONTINUE
C      FUNK=SQRT(FUNK/(N-1))
C      RETURN
C      END
C
```

```
C   This function is where the function that you wish to
C   solve the parameters for will go in.
C
C   Attach this function to the main part of the program
C   that you write for input and output of your data
C
CCCC
```

```
      JW=1
      JB=1
      DO 30 I=2,NV
      IF (RI(I).GE.WR)  WR=RI(I)
      IF (RI(I).GE.WR)  JW=I
      IF (RI(I).LT.BR)  BR=RI(I)
      IF (RI(I).LT.BR)  JB=I
   30 CONTINUE
      IF ((KI.GE.KX).OR.(BR.LT.EP))  GO TO 110
      IF (((WR-BR)/BR).LT.EP)  GO TO 110
      KI=KI+1
      IF (BR.NE.PR)  PR=BR
      F=1.0
      CALL VERTIX(S,T,JW,NP,F,H,B,R,NC,N,NS)
      IF (R.GT.BR)  GO TO 40
      RT=R
      DO 50 I=1,NP
      TT(I)=T(I)
   50 CONTINUE
      F=2.0
      CALL VERTIX(S,T,JW,NP,F,H,B,R,NC,N,NS)
      IF (R.GT.RT) GO TO 60
```

```
 90 DO 70 I=1,NP
    S(I,JW)=T(I)
 70 CONTINUE
    RI(JW)=R
    GO TO 20
 60 R=RT
    DO 80 I=1,NP
    T(I)=TT(I)
 80 CONTINUE
    GO TO 90
 40 IF (R.LE.WR)  GO TO 90
    F=-0.5
    CALL VERTIX(S,T,JW,NP,F,H,B,R,NC,N,NS)
    IF (R.LE.WR)  GO TO 90
    DO 100 I=1,NP
    DO 100 J=1,NV
    IF (J.NE.JB)  S(I,J)=(S(I,JB)+S(I,J))/2
100 CONTINUE
    GO TO 20
110 IF (KI.GE.KX) WRITE (6,120)
    IF (KI.LT.KX) WRITE (6,130)
120 FORMAT (/5X,'MAXIMUM NUMBER OF LOOPS EXCEEDED',/)
```

```
  130 FORMAT (/5X,'CONVERGENCE CRITERIA REACHED',/)
      RETURN
      END
CCCC
```

```
   50 CONTINUE
      R=FUNK(H,T,B,NC,N,NS)
      RI(I)=R
   40 CONTINUE
      RETURN
      END
CCCC
```

```
      C(I)=SU/NP
   30 T(I)=C(I)*(1.0+F)-F*S(I,JW)
   10 CONTINUE
      R=FUNK(H,T,B,NC,N,NS)
      RETURN
      END
```

## REFERENCE LIST


1. Thomas, J.M. *Scientific American* **1992** (April), 112.

2. National Research Council *Catalysis Looks to the Future*; National Academy Press: Washington, D.C., 1992.

3. Tenabe, K.; Hattori, H.; Yamaguchi, T.; Tanaka, T. *Acid-Base Catalysis*; VCH Publishers: New York, 1989.

4. Parry, E.P. *J. Catal.* **1963**, *2*, 371.

5. Curthoys, G.; Davydov, V.; Kiselev, A.V.; Kiselev, S.A.; Kuznetsov, B.V. *J. Colloid Interface Sci.* **1974**, *48*, 58.

6. a.) Dawson, W.H.; Kaiser, S.W.; Ellis, P.D.; Inners, R.R. *J. Phys. Chem.* **1982**, *86*, 867.
   b.) Duncan, T.M.; Winslow, P.; Bell, A.T. *Chem. Phys. Lett.* **1983**, *102*, 163.
   c.) Batamack, P.; Doremieux-Morin, C.; Fraissard, J.; Freude, D. *J. Phys. Chem.* **1991**, *95*, 3790.
   d.) Batamack, P.; Doremieux-Morin, C.; Vincent, R.; Fraissard, J. *Chem. Phys. Lett.* **1991**, *180*, 545.

7. Klinowski, J. *Chem. Rev.* **1991**, *91*, 1459.

8. Fierro, J.L.G. *Spectroscopic Characterization of Heterogeneous Catalysts Part B: Chemisorption of Probe Molecules*; Elsevier: New York, 1990.

9. Gravelle, P.C. *Catal. Rev-Sci. Eng.* **1977**, *16*(1), 37.

10. Fowkes, F.W.; McCarthy, D.C.; Tischler, D.O. *Polymer Science and Technology, Vol. 27 (Mol. Charact. compos. Interfaces)*; Plenum Press: New York, 1983; pp. 401-411.

11. Arnett, E.M.; Cassidy, K.F. *Rev. Chem. Intermed.* **1988**, *9*, 27.

12. Lim, Y.Y.; Drago, R.S.; Babich, M.W.; Wong, N.; Doan, P.E. *J. Am. Chem. Soc.* **1987**, *109*, 169.

13. a.) Drago, R.S. *Coord. Chem. Rev.* **1980**, *33*, 251.
b.) Drago, R.S.; Ferris, D.C.; Wong, N. *J. Am. Chem. Soc.* **1990**, *112*, 8953.
c.) Drago, R.S.; Vogel, G.C.; Dadmun, A.P. *Inorg. Chem.* **1993**, *32*, 2473.

14. Adamson, A.W. *Physical Chemistry of Surfaces*; 5th Ed.; Interscience: New York, 1990.

15. a.) McDonald, R.A. *J. Phys. Chem.* **1958**, *62*, 1168.
b.) Morrow, B.A.; McFarlan, A.J. *J. Non-Cryst. Solids* **1990**, *120*, 61.

16. Bronnimann, C.E.; Zeigler, R.C.; Maciel, G.E. *J. Am. Chem. Soc.* **1988**, *110*, 2023.

17. Feher, F.J.; Newman, D.A. *J. Am. Chem. Soc.* **1990**, *112*, 1931.

18. Hench, L.L.; West, J.K. *Chem. Rev.* **1990**, *90*, 33.

19. *CRC Handbook of Chemistry and Physics*; 71st, Ed.; Lide, D.R.; CRC Press: Boston, 1990.

20. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; 2nd Ed.; VCH: Weinheim, Federal Republic of Germany, New York, NY, 1984.

21. Cardona-Martinez, N.; Dumesic, J.A. *J. Catal.* **1990**, *125*, 427.

22. a.) Drago, R.S.; Getty, E.E. U.S. Patent No. 4,719,190, Jan. 12, 1988.
b.) Drago, R.S.; Getty, E.E. U.S. Patent No. 4,929,800, May 29, 1990.

23. a.) Drago, R.S.; Getty, E.E. *J. Am. Chem. Soc.* **1988**, *110*, 3311.
b.) Drago, R.S.; Getty, E.E. *Inorg. Chem.* **1990**, *29*, 1186.

24. Drago, R.S.; Petrosius, S.C.; Chronister, C.W. *Inorg. Chem.* **1994**, *33*, 367.

25. Getty, E.E.; Petrosius, S.C.; Drago, R.S. *J. Mol. Cat.* **1991**, *67*, 127.

26. Hair, M.L. *Infrared Spectroscopy in Surface Chemistry*; Marcel Dekker, Inc.: New York, 1967.

27. Getty, E.E. Ph.D. Dissertation, University of Florida, 1988.

28. Chronister, C.W.; Drago, R.S. *J. Am. Chem. Soc.* **1993**, *115*, 4793.

29. Morcom, K.W.; Travers, D.N. *Trans. Faraday Soc.* **1966**, *63*, 2063.

30. a.) Hayashi, H.; Moffat, J.B. *J. Catal.* **1982**, *77*, 473.
b.) Saito, Y.; Cook, P.N.; Niiyama, H.; Echigoya, E. *J. Catal.* **1985**, *95*, 49.

31. Izume, Y.; Hasebe, R.; Urabe, K. *J. Catal.* **1983**, *84*, 402.

32. Ghosh, A.K.; Moffat, J.B. *J. Catal.* **1986**, *101*, 238.

33. Misono, M. *Catal. Rev.-Sci. Eng.* **1987**, *29*(2&3), 269.

34. Vit, Z. *React. Kinet. Catal. Lett.* **1986**, *32*(1), 205.

35. Pope, M.T. *Heteropoly and Isopoly Metalates*; Springer-Verlag: Berlin; New York, 1983.

36. a.) Drago, R.S. *Coord. Chem. Rev.* **1980**, *33*, 251.
b.) Drago, R.S.; Ferris, D.C.; Wong, N. *J. Am. Chem. Soc.* **1990**, *112*, 8953.
c.) Drago, R.S.; Vogel, G.C.; Dadmun, A.P. *Inorg. Chem.* **1993**, *32*, 2473.

37. Parry, E.P. *J. Catal.* **1963**, *2*, 371.

38. Highfield, J.G.; Moffat, J.B. *J. Catal.* **1984**, *89*, 185.

39. Perrin, D.D. *Purification of Laboratory Chemicals*; 3rd ed.; Pergamon Press: Oxford; New York, 1988.

40. Drago, R.S.; Chronister, C.W.; Ferris, D.F.; Jurczyk, K. *Proceedings of the 1992 ERDEC Scientific Conference on Chemical Defense Research*; 17-20 November 1992.

41. Okuhara, T.; Hashimoto, T.; Hibi, T.; Misono, M. *J. Catal.* **1985**, *93*, 224, and references therein.

42. Davis, M.E. *Acc. Chem. Res.* **1993**, *26*, 111.

43. Breck, D.W. *Zeolite Molecular Sieves* John Wiley & Sons: New York, 1974.

44. Olson, D.H.; Dempsey, E. *J. Catal.* **1969**, *13*, 221.

45. Sun, T.; Seff, K. *J. Catal.* **1992**, *138*, 405.

46. a.) Uytterhoeven, J.B.; Christner, L.G.; Hall, W.K. *J. Phys. Chem.* **1965**, *69*(6), 2117.
b.) Jacobs, P.A.; Uytterhoeven, J.B. *J. Chem. Soc., Faraday Trans. I* **1973**, *69*, 359.

c.) Hughes, T.R.; White, H.M. *J. Phys. Chem.* **1967**, *71*(7), 2192.
d.) Angell, C.L.; Schaffer, P.C. *J. Phys. Chem.* **1965**, *69*(10), 3463.

47. Ward, J.W. *J. Catal.* **1967**, *9*, 225.

48. Klinowski, J. *Chem. Rev.* **1991**, *91*(7), 1466.

49. a.) Michel, D.; Germanus, A.; Pfeifer, H. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 237.
b.) Ripmeester, J.A. *J. Am. Chem. Soc.* **1983**, *105*, 2925.
c.) Maciel, G.E.; Haw, J.F.; Chuang, I.-S., Hawkins, B.L.; Early, T.L.; McKay, D.R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529.
d.) Haw, J.F.; Chuang, I.-S.; Hawkins, B.L.; Maciel, G.E. *J. Am. Chem. Soc.* **1983**, *105*, 7206.

50. a.) Lunsford, J.H.; Rothwell, W.P.; Shen, W. *J. Am. Chem Soc.* **1985**, *107*, 1540.
b.) Baltusis, L.; Frye, J.S.; Maciel, G.E. *J. Am. Chem. Soc.* **1986**, *108*, 7119.

51. a.) Hashimoto, K.; Masuda, T.; Mori, T. *New Developments in Zeolite Science and Technology* ed. Murakami, Y.; Iijima, A.; Ward, J.W., Elsevier: New York, 1986, 503.
b.) Quanzhi, L.; Ruiming, Z.; Zhiyuan, X. ibid. p. 487.

52. Choudhary, V.R.; Singh, A.P.; Kumar, R. *J. Catal.* **1991**, *129*, 293.

53. a.) Auroux, A.; Bolis, V.; Wierzchowski, P.; Gravelle, P.C.; Vedrine, J.C. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*(11), 2544.
b.) Zhi, C.S.; Auroux, A.; Taarit, Y.B. *Can. J. Chem.* **1988**, *66*, 1013.
c.) Krivanek, M.; Nguyen, T.D.; Jiru, P. *Thermochim. Acta* **1987**, *115*, 91.

54. Zecchina, A.; Arean, C.O. *Catal. Rev.-Sci. Eng.* **1993**, *35*(2), 261.

## BIOGRAPHICAL SKETCH

Chris W. Chronister was born in Hanover, Pennsylvania, on June 27, 1967, to Elven and Betty Chronister. He attended Hanover High School and graduated in June 1985. In the fall of 1985, he enrolled at the Florida Institute of Technology, Jensen Beach Campus. After one year there, this branch campus closed and he moved to the main campus in Melbourne, Florida. Upon transferring, his major changed from manufacturing technology to chemistry. He conducted senior research under the guidance of Dr. J. Clayton Baum on the photochemistry of a carbazole-acridine energy transfer "sink effect." In August 1989 he graduated from the Florida Institute of Technology with a Bachelor of Science degree in chemistry.

By the end of August 1989, Chris started his graduate study at the University of Florida. There he worked for Dr. Russell S. Drago on the development of a novel calorimetric-adsorption (cal-ad) method for the determination of surface acidity. Upon receiving the degree of Doctor of Philosophy in inorganic chemistry he plans to join Dr. Thomas J. Meyer at the University of North Carolina, Chapel Hill, as a postdoctoral fellow.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Russell S. Drago, Chair
Graduate Research Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James M. Boncella
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Daniel R. Talham
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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